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STUDY OF THE REACTION KINETICS OF THE RECIPROCAL TRANSFORMATION OF SATURATED PHOSPHOMOLYBDIC AND LUTEOPHOSPHOMOLYBDIC ACIDS

E. A. Nikitina and O. N. Sokolova

Phospho-9-molybdic acid (luteophosphomolybdic acid) is produced in aqueous solution by the action of phosphoric acid on phosphomolybdic acid of the saturated series. As our earlier investigation showed [1], the reaction is reversible, and its direction depends on the temperature and on the concentration of H_3PO_4.

$$3H_7[P(Mo_2O_7)_6] + H_3PO_4 \rightleftharpoons 2H_{12}[P_2O_5(Mo_2O_7)_3].$$

We found, experimentally, that an excess of 160% phosphoric acid and a temperature of about 20° are most favorable for the forward reaction; the reverse process was accelerated appreciably at a temperature above 30°.

In 1951, Souchay and Focherre [2] studied the transformation of saturated phosphomolybdic acid to the compound of the luteo series at 25°, namely they studied: the rate of the transformation in aqueous solution, in the presence of nitric acid, in the presence of an excess of sodium phosphate, and in a partially neutralized solution. The experiments were continued for about 1000 hours. It was found that an increase of the phosphate-ion concentration accelerates the process somewhat, but does not seem to be a decisive factor in the displacement of the equilibrium; an excess of a minerald acid had no effect on the transformation, but partial neutralization represses the formation of luteophosphomolybdic acid. Souchay and Focherre were unable to establish the reversibility of the reaction between phosphoric and saturated phosphomolybdic acids, and assumed that in this case it was not possible to speak of an equilibrium in the thermodynamic sense of the word; they assumed that in this reaction equilibrium is established after approximately 1008 hours. The authors were unable to determine the order of the reaction.

We posed for ourselves the problem of studying the relationship of the reaction rate, in the formation of luteophosphomolybdic acid, to the concentration of phosphoric and saturated phosphomolybdic acids in the initial solution, and to the temperature.

EXPERIMENTAL

Study of the reaction kinetics of the transformation of saturated phosphomolybdic acid to the luteo form. The investigations were carried out in a thermostat at 0 and 25°.

Saturated phosphomolybdic acid,* for all the experiments, was synthesized by a method [3] described earlier. Solutions of different concentrations were prepared from the acid obtained; to some of the solutions we added the theoretical amount of phosphoric acid and ot others we added an excess (160% as compared with that calculated from the equation).

After a time, luteophosphomolybdic acid appeared in solution, and at the same time the content of saturated phosphomolybdic acid decreased. In order to establish the course of the process, we observed the changes in the compositions of the solutions; weighed portions of the solutions were withdrawn after certain time intervals and the saturated phosphomolybdic acid contents in them were determined.

For this purpose, from 2 to 10 ml of solution was withdrawn into a beaker for weighing, the quantity taken depending on the saturated phosphomolybdic acid content; the beaker and cover were weighed, and an equal volume of a saturated solution af ammonium chloride was poured into the beaker. The precipitated ammonium salt of saturated phosphomolybdic acid was filtered through a crucible fitted with a No. 4 porous plate; the precipitate, in some of the same ammonium chloride solution, was transferred to a filter and washed, first with a more concentrated, 13-14%, solution of NH_4Cl, and then with a more dilute solution; for the final washing we used a solution containing 0.4-0.5% ammonium chloride. The precipitate was washed 3 times with 10 ml portions of each solution; the precipitate could not be washed with water, since this converts it to the colloidal condition and it passes through the filter. The crucible with the precipitate was dried for 1 hour at 100-110°, and then it was dried to constant weight at 130-140°. The saturated phosphomolybdic acid content in the solution was calculated from the quantity of salt obtained.

In the first part of the work, duplicate analyses of the solutions existing at 25 and 0° were carried out under room temperature conditions.

* The saturated phosphomolybdic acid in the tables and in the figures is abbreviated as s.p.m..

TABLE 1

Kinetics of the Transformation of Saturated Phosphomolybdic Acid to the Luteo Form

No. of days	Acid concentration s. p. m. (wt. %)	s. p. m. (mole %)	phosphoric (wt. %)	phosphoric (mole %)	No. of days	Acid concentration s. p. m. (wt. %)	s. p. m. (mole %)	phosphoric (wt. %)	phosphoric (mole %)
	Temperature 25°					Temperature 0°			
0	17.5	0.2095	0.3059	0.03817	0	49.30	0.9886	2.902	1.117
5	9.46	0.1113	0.1648	0.03345	1	19.36	0.2373	2.387	0.5558
7	7.90	0.08296	0.1375	0.02743	2	14.96	0.1736	2.310	0.5092
18	3.52	0.03527	0.06063	0.01154	4	8.31	0.1124	2.193	0.4475
45	0.39	0.00378	0.005714	0.001053	8	3.00	0.03043	2.100	0.4046
98	0.37	0.00359	0.00561	0.001034	40	0.53	0.00524	2.056	0.3862
0	17.50	0.2053	1.074	0.2408	72	0.46	0.00454	2.055	0.3857
1	17.30	0.0820	0.8812	0.2658	113	0.50	—	—	—
5	1.65	0.0103	0.7985	0.1501	0	47.64	0.9118	2.8314	1.0295
7	1.36	0.0134	0.7935	0.1486	1	15.05	0.1747	2.2587	0.4983
11	0.86	0.00843	0.7847	0.1462	2	13.44	0.1531	2.2305	0.4827
17	0.36	0.00351	0.7759	0.1439	4	12.71	0.1435	2.2177	0.4747
45	practically none	—	—	—	8	8.95	0.0938	2.1517	0.4421
					10	6.48	0.0682	2.1083	0.4210
0	34.68	0.5242	2.084	0.5997	26	3.28	0.0834	2.0523	0.3965
1	14.61	0.1679	1.751	0.3823	33	2.03	0.0204	1.8325	0.3488
5	4.64	0.04766	1.576	0.3076	67	1.02	0.0101	1.6555	0.3114
7	0.40	0.00431	1.501	0.2800	85	0.90	0.00888	1.6532	0.3099
17	0.59	—	—	—					
45	practically none	—	—	—					

However, the results of the analyses obtained for the solution at 0° were unreliable and were too high with respect to the saturated phosphomolybdic acid content, which at first prevented the construction of a graph of the process.

It has been noted that the reaction of the reciprocal transformation of the two phosphomolybdic acids is reversible. Obviously, fluctuation of the temperature of the solutions from zero to room temperature during the analyses, shifted the equilibrium toward the formation of saturated phosphomolybdic acid, resulting in elevated values for the concentrations of the latter in the solutions studied.

It was necessary to eliminate the temperature fluctuations of the solutions, i.e., to carry out the analyses at 0°. Above all, we wanted to avoid the operation of weighing the sample; therefore, in subsequent experiments we simultaneously withdrew two samples of solution, using calibrated pipettes. One sample was placed in a beaker under the usual conditions and weighed; the other sample, of equal volume, was withdrawn into a beaker which had previously been kept at 0° for 0.5 hour. To the samples in the cold, we added a solution of ammonium chloride (saturated at the desired temperature) which had been cooled to 0°.

The precipitate of the ammonium salt of saturated phosphomolybdic acid was quickly transferred to a crucible with a porous bottom; the crucible had previously been kept at 0° for 0.5 hour. The precipitate was filtered and washed at 0°; the ammonium chloride solutions had been cooled to 0°. With the observance of these conditions, the results of the analyses were entirely satisfactory.

The experimental conditions and the results of the investigations are presented in Table 1 (Fig. 1).

From the data of Table 1 it is evident that, in the presence of an excess of phosphoric acid, most of the saturated phosphomolybdic acid is converted to the luteo form during the first 6-7 days, but a considerable time is required for complete transformation.

To determine the order of the reaction for the transformation of saturated phosphomolybdic acid to the luteo form, we calculated the values of the constant from the usual equation, for all the experiments of the five series.

$$\text{For monomolecular reactions } K = \frac{2.303}{t} \cdot \frac{a}{a-x},$$

For bimolecular $K = \frac{2.303}{t(a-b)} \cdot \frac{b(a-x)}{a(b-x)}$.

The values obtained for the constant are presented in Table 2.

In order to derive the average values of the constant from the equation for a 1st order reaction, we excluded the following two experiments: experiment 3 from series III and experiment 1 from series V.

From the data obtained, we concluded that in the three series of experiments carried out at 25°, with the optimum excess of phosphoric acid in the reaction system (II, III, and IV series), the average values of the constant agreed satisfactorily: 0.248, 0.255 and 0.336.

For the experiments of series V, carried out at 0°, the average value of the constant was smaller, amounting to 0.144; for series I experiments, in which the phosphoric acid was present in the theoretically calculated quantity, the average value of the constant was 0.554.

Calculation of the values of the constant completely confirmed our many observations of the process of synthesis of luteophosphomolybdic acid: with the theoretically calculated quantity of phosphoric acid, the process proceeds more slowly than would be indicated by the low value of the constant; with an excess of phosphoric acid the reaction proceeds more rapidly – the value of the constant increases.

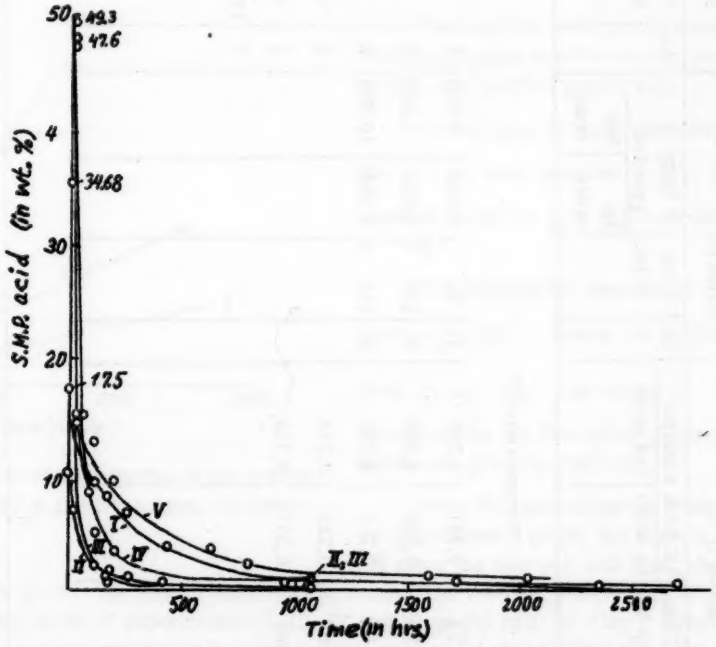

Fig. 1. Kinetics of the conversion of saturated phosphomolybdic acid to the luteo form. Explanation in the text.

Later, we calculated the average value of the constant from the equation for a bimolecular reaction. We eliminated four experiments (5 from series I, 3 from series III, 1 and 2 from series V) but, in spite of this, for the four series of experiments carried out with an excess of phosphoric acid, we obtained highly divergent values for the constant: 4.964, 1.980, 1.145 and 0.911.

On calculation of the constant for the series I experiments, it was found that the values of the constant, as calculated from the equations for reactions of the 1st and 2nd orders, agreed rather closely: 0.0554 and 0.0745 (Table 2).

We determined the half-life period of the reactions for all five series of experiments. For series II, III and IV, carried out under identical temperature conditions, the half-life periods were: 18.85 hours, 20.73 hours and 19.76 hours, which gives an average value of 19.78 hours; the corresponding concentrations of saturated phosphomolybdic acid in the original solutions were 17.5, 34.68 and 49.3 wt.%. Consequently, under the conditions specified the half-life period of the reaction did not depend on the concentration of the substance in the original solution; this confirmed the assumption that the reaction studied might belong to the first order.

TABLE 2

Calculation of the Rate Constant of the Transformation of Saturated Phosphomolybdic Acid to the Luteo Form

Series I				Series II				Series III				Series IV				Series V			
No.	Time in hrs.	K from equation		No.	Time in hrs.	K from equation		No.	Time in hrs.	K from equation		No.	Time in hours	K from equation		No.	Time in hrs.	K from equation	
		1st order	2nd order			1st order	2nd order			1st order	2nd order			1st order	2nd order			1st order	2nd order
																Temperature 0°			
						Temperature 25°													
1	120	0.0391	0.1390	1	24	0.241	6.271	1	24	0.299	2.530	1	24	0.404	1.697	1	24	0.500*	2.059*
2	168	0.0341	0.0990	2	120	0.242	4.383	2	120	0.211	1.434	2	48	0.276	1.062	2	48	0.286	1.138*
3	432	0.0312	0.0417	3	168	0.211	3.772	3	168	1.668*	10.320	3	96	0.213	0.721	3	96	0.152	0.597
4	1080	0.1164	0.0183	4	264	0.213	3.755					4	192	0.393	1.204	4	192	0.113	0.412
5	2342	0.0561	0.0081*	5	408	0.331	5.728					5	960	0.457	1.335	5	240	0.128	0.446
												6	1728	0.293	0.854	6	624	0.101	0.330
																7	792	0.130	0.375
																8	1608	0.129	0.332
																9	2040	0.116	0.296
Average Value . . .		0.0554	0.0745	–	–	0.248	4.964	–	–	0.255	1.980	–	–	0.336	1.145	–	–	0.144	0.411

* Values which were not considered in the calculation of the average value of the constant from the equations given.

The value found for the half-life period of the reaction, for the series of experiments carried out at 0°, was 17.54 hours, i.e., it was somewhat less than the average value of the half-life period of the reaction for the three series of experiments indicated above.

For series I experiments, carried out with the theoretically calculated quantity of phosphoric acid, the half-life period of the reaction was considerably higher, namely, 141 hours.

For this series of experiments, the value of the constant calculated from the equation for 1st order reactions was 0.0049, but for 2nd order reactions it was 0.0343. Consequently, under the conditions indicated, the transformation of saturated phosphomolybdic acid to the luteo form corresponded closely to a 2nd order reaction.

Calculation of the constant from the equation for 3rd order reactions gave completely inadmissible results.

The data obtained allowed us to assume that the transformation of saturated phosphomolybdic acid to the luteo form was a 1st order reaction. However, it should be considered that, as the concentration of phosphoric acid in the reaction system (series I) decreased, a change of the reaction order to that of a bimolecular reaction was observed.

The fact that complete transformation of saturated phosphomolybdic acid to the luteo form was attained in two series of experiments (II and III) permits us to assume that the reaction, under certain conditions, goes practically to completion.

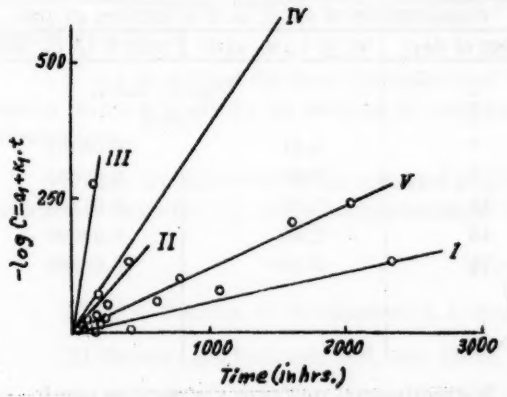

Fig. 2. Values of −log C of the kinetics of the conversion of the saturated acid to the luteo form. Explanation in the text.

The reaction order of the conversion of saturated phosphomolybdic acid to the compound of the luteo series was also verified graphically.

On the basis of the differential equation for the rate of a 1st order reaction $-\frac{dC}{dt} = k_1 C$ we found the equation $-\log C = a_1 + k_1 t$, and calculated the values of −log C.

The differential equation of the 2nd order has the form: $-\frac{dC}{dt} = k_2 C^2$, hence, the solution of the equation gives $\frac{1}{C} = a_2 + k_2 t$. The values of −log C and $\frac{1}{C}$ were calculated for all five series of experiments; the calculations are given in Table 3.

From the calculations of −log C and 1/C (Table 3) we constructed a graph; the time in hours was designated along the abscissa, and along the ordinate, the values of −log C and 1/C were given. For series I experiments, a straighter line was obtained on the basis of the 1/C values, but for the remaining series of experiments (II, III, IV and V) on the basis of −log C values (Figs. 2 and 3). Therefore, we reached the same conclusion by the graphical method for determining the order of reaction, i.e., that the reaction studied belongs to the 1st order.

Study of the kinetics of the decomposition of luteophosphomolybdic acid. We studied the effect of concentration and temperature on the process of conversion of the luteophosphomolybdic acid to the saturated acid in solution.

The investigations were carried out in a thermostat at 0 and 25°; the concentrations of luteophosphomolybdic acid in the solutions were 17.3 and 49.45 wt. %.

Observations of the composition changes of the solutions were made by determining the contents of saturated phosphomolbydic acid in them, in a way similar to that described above.

Solutions of luteophosphomolybdic acid at 0° did not change over a period of almost 4 months.

The results of the investigations at 25° are given in Table 4, (Fig. 4).

By investigation of the relation of temperature and concentration to the kinetics of the decomposition reaction of luteophosphomolybdic acid in aqueous solution, we were able to account for the fact that, on evaporation of the aqueous solutions of the luteophosphomolybdic acid, we were unable to obtain a preparation which was free from concentrated phosphomolybdic acid.

TABLE 3

Calculation of the Values of $-\log C$ and $1/C$ for Data from the Study of the Reaction Rates of the Conversion of Saturated Phosphomolybdic Acid to the Compound of the Luteo Series

No.	Series I experiments		Series II experiments		Series III experiments		Series IV experiments		Series V experiments	
	$-\log C$	$\frac{1}{C}$	$-\log C$	$\frac{1}{C}$	$-\log C$	$\frac{1}{C}$	$-\log C$	$\frac{1}{C}$	$-\log C$	$\frac{1}{C}$
1	4.803	16.79	5.866	150.58	7.346	60.89	9.933	40.97	12.17	49.59
2	5.18	16.71	29.056	525.97	25.32	172.03	13.32	51.15	13.98	54.62
3	13.514	18.04	35.461	633.70	280.23	1733.8	20.56	69.33	14.630	57.90
4	84.03	19.77	56.24	966.6	–	–	75.49	232.2	21.80	79.20
5	131.39	18.97	135.05	2336.02	–	–	438.77	1281.6	30.79	107.7
6	–	–	–	–	–	–	506.31	3203	63.06	206.2
7	–	–	–	–	–	–	–	–	102.98	297.0
8	–	–	–	–	–	–	–	–	207.44	533.86
9	–	–	–	–	–	–	–	–	236.64	603.84

TABLE 4

Kinetics of the Decomposition of Luteophosphomolybdic Acid at 25°

Concentration of l.p.m.* acid in solution 17.3%			Concentration of l.p.m. acid in solution 49.45%		
number of days	wt. % l.p.m. acid	mole % l.p.m. acid	number of days	wt. % l.p.m. acid	mole % l.p.m. acid
2	Not observed		1	Slightly turbid	
4	Slightly turbid		2	Turbid	
6			6	0.31	0.00301
11	0.18	0.00174	7	0.58	0.00564
14	0.22	0.00213	14	1.19	0.01164
43	0.35	0.00395	43	2.94	0.02927
74	0.66	0.00642	74	5.19**	0.05289
103	1.19	0.01014			
138	1.52	0.01492			
210	2.37	0.02347			

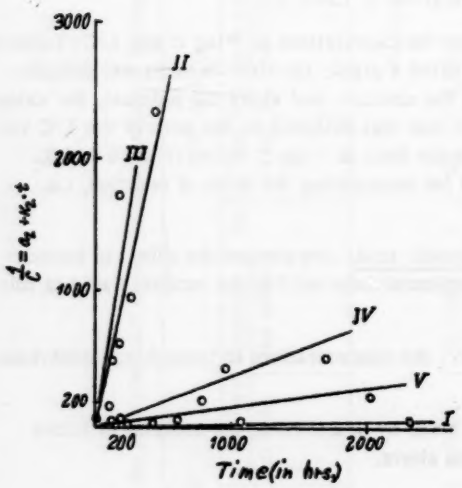

Fig. 3. Values of 1/C of the kinetics of the conversion of the saturated acid to the luteo form. Explanation in the text.

In experimental studies on the reaction rate it was found that, as the concentration of the solution increased, the rate of formation of saturated phosphomolybdic acid increased, and this in turn caused an increase of the saturated phosphomolybdic acid content in solutions of luteophosphomolybdic acid, depending on the extent to which the latter were concentrated by evaporation.

The decomposition curves of luteophosphomolybdic acid were of a linear character; the reaction rate of the decomposition of the hetero-polyacid increased appreciably in the more concentrated solutions (Fig. 4).

A study of the reaction rate of the transformation of saturated phosphomolybdic acid to the compound of the luteo series showed that it was a 1st order reaction; the established reaction order, characteristic of polymerization processes, confirmed the validity of the structuralformula of luteophosphomolybdic acid as a binuclear complex. Thus, this physico-chemical investigation constitutes a new confirmation of the coordination theory of the structure of hetero-polycompounds.

* l.p.m. equals luteophosphomolybdic acid.

** On the 74th day, molybdic acid appeared in the solution, i.e., the complex began to break down.

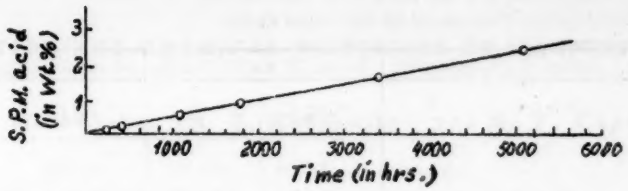

Fig. 4. Kinetics of the conversion of luteophosphomolybdic acid to the saturated form.

SUMMARY

1. The reaction kinetics of the conversion of saturated phosphomolybdic acid to the compound of the luteo series was studied at 0 and 25°.

2. The order of the reaction was established by graphical methods, by calculation of the reaction rate constant and by determination of the half-life period of the reaction.

3. The reaction studied was shown to be of the 1st order.

4. The reaction kinetics of the conversion of luteophosphomolybdic acid to the saturated compound was studied at 0 and 25°.

5. We established the linear dependence of the rate of the latter reaction on concentration at 25°. At 0°, over a period of 4 months, we observed no transformation of phospho-9-molybdic acid to the compound of the saturated series.

6. The transformation of the saturated acid to a compound of the 9th series should be considered as a polymerization reaction, i.e., as the transformation of a mononuclear to a binuclear complex.

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COMPOSITION AND CHEMICAL PROPERTIES OF MAGNESIUM BORIDES

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The first reference to the magnesium borides is in the work of Geuter [1], who obtained them by reduction of sodium borofluoride with metallic magnesium. Later, the product to which the formula Mg_3B_2 was attributed was produced by Jones [2] and by Jones and Taylor [3], by the reduction of boric anhydride with magnesium, by the reaction of the elements, and by the reaction of magnesium with BCl_3. This result was confirmed by Moissan in 1895 in his work on the study of methods of obtaining elementary boron [4]. However, Moissan observed that, besides the boride which easily decomposed in water and acids with the evolution of gaseous boron hydrides, there also exists another stable magnesium boride which is not decomposed even on prolonged treatment with acids. This boride is one of the most difficultly removed impurities in amorphous boron, and accordingly [4] can be decomposed by fusion with an excess of boric anhydride.

In 1914, Ray [5] confirmed the foregoing data on the composition of magnesium boride (Mg_3B_2), maintaining that the boride of a different composition did not exist. This point of view was maintained in subsequent generally recognized works, especially after the work of Stock and coworkers [6, 7], who were engaged in the study of the properties of magnesium boride as a raw material for the production of boron hydrides [8, 9, 10]. However, data in the work of Travers and Ray [11] contradict such a composition for magnesium boride. The results of their study of the products of the hydrolysis of magnesium boride showed the inadequacy of the formula Mg_3B_2, which compelled the authors to advance a hypothesis concerning the existence of a boride of the composition Mg_2B_4.

Physico-chemical data relative to the properties of magnesium boride and to its structure were lacking until recently. No earlier than 1953 and 1954, two foreign reports [12, 13] pertaining to the structure of magnesium diboride appeared, confirming our results.

The purpose of the present report was the study of the system Mg—B, and also the study of the properties of the individual compounds forming in the system. The difficulties in the investigation of this system related to the volatility of magnesium, the impossibility of obtaining monocrystals of the binary compounds observed, and also inconveniences of an analytical nature, which prevented us from carrying out a separate determination of elementary and combined boron; for the present, all this made it impossible to completely clarify the problem of the composition and structure of the boride phases with high boron contents. However, we did obtain conclusive results for magnesium diboride.

EXPERIMENTAL

Procedure. Different compositions of borides were prepared from powders of amorphous boron and magnesium. The amorphous boron contained 98% of the primary substance, 1.4% Mg, 1.1% Fe + Al and 0.3% Si.

The magnesium contained the following impurities: 0.1% Al, 0.07% Fe and 0.05% Si.

The powdered components, in fixed proportions, were carefully mixed in an agate mortar and poured into a graphite test tube, in which they were either pressed manually, or briquetted under a pressure of 800 kg/cm^2. The graphite test tube and its contents were heated in an atmosphere of carefully purified hydrogen; the heating was carried out in cylindrical iron reaction vessels or in hermetically sealed quartz reaction vessels, from which the air had been previously evacuated, and the charge was degasified at a temperature of about 150°. The reactors were placed in a heated crucible furnace and kept there for the required time at a fixed temperature, after which they were cooled rapidly in cold water. The heating temperature was measured in the reaction zone by means of a Pt—Pt/Rh thermocouple. Because of its marked exothermicity, the reaction between boron and magnesium could always be detected by the rapid temperature change.

By a preliminary chemical analysis and an X-ray investigation, the absence of a reaction between the graphite and the components of the charge was demonstrated.

The black or dark-cinnamon colored agglomerates obtained as a result of the reaction with different proportions of Mg and B, were subjected to X-ray and chemical analysis.

The X-ray structural investigation was carried out with $Fe K_\alpha$ -radiation in a chamber with an adapter diameter of 57.3 mm; the most typical samples were photographed in a VRS chamber with an adapter diameter of 143.2 mm.

We carried out a separate chemical analysis for the soluble and insoluble portions of the product. For the analysis of the soluble borides, in order to eliminate the possibility of the loss of gaseous products, the decomposition with nitric acid was carried out in sealed glass tubes at 150° for 48 hours. The insoluble borides were converted to the soluble form by fusion with carbonates mixed with sodium nitrate.

Boron was determined volumetrically by titration with 0.1 N $Ba(OH)_2$ in the presence of mannitol; magnesium was determined by the pyrophosphate method after removal of H_3BO_3. Free, uncombined magnesium was determined by vacuum distillation at 450°.

The specific gravity of the finely-ground (-100μ) powdered borides was determined pyknometrically in benzene.

TABLE 1

Phase Composition of the Reaction Products of Magnesium and Boron

Molar ratio	Reaction temperature	Phase composition on basis of X-ray data
2:1	800°	MgB_2 + considerable quantity of magnesium
3:2	800	MgB_2 + considerable quantity of magnesium
	1140	A + B
1:1	800	MgB_2 + Mg contamination
3:4	800	MgB_2 + Mg contamination
1:2	600	Magnesium + traces of MgB_2
	700	MgB_2 + magnesium contamination
	800	MgB_2
	960	A + MgB_2
	1000	A + traces of MgB_2
	1050	A + B
	1200	C
1:4	900	A
	1000	A
	1060	A
	1200	C
1:6	800	Dispersed line MgB_2 + boron line
	1000	A
	1200	B

TABLE 2

Phase Composition of the Thermal Decomposition Products of MgB_2

Calcination temperature	Length of time of calcination (hours)	Percent insoluble residue in calcination products	Phase composition of product on basis of X-ray data
800°	2	6.2	MgB_2
900	4	24.5	MgB_2 + traces of boride A
1000	2	81.3	Boride A + traces of MgB_2
1140	2	86.1	Mixtures of borides A & B
1200	2	92.6	Boride C
1300	2	–	Boride C
1400	2	–	Boride C
1500	4 (in vacuo)	–	Boride C

Phase analysis of the reaction products of magnesium and boron. An X-ray investigation of the reaction products of magnesium and boron with Mg to B molar ratios of 2:1, 3:2, 1:1, 1:2, 1:4, 1:6 and at temperatures from 800 to 1200°, showed that the phase composition of the reaction products in the experiments with 2-hour heating (Table 1), depends almost exclusively on the reaction temperature, and not on the ratios of the components of the charge.

The visible reaction between magnesium and boron, during which the diboride phase, MgB_2, was always produced at low temperatures, began at a temperature of 720 ± 20° C. At elevated reaction temperatures, new phases, designated as the A, B and C phases, formed one after the other, and were characterized, as will be seen later, by elevated boron contents. From the data of Table 2, it is obvious that this is connected with the thermal decomposition of MgB_2.

The phase compositions of the different reaction products of Mg with B are characterized by the X-ray photographs presented in Fig. 1 [see plate, page 607]. The data of Table 2 show the extraordinary thermal stability of phase C, which will be considered in greater detail below.

The boride of MgB_2 composition. Magnesium diboride is a dark-cinnamon colored powder, the specific gravity of which varies from 2.48 to 2.67 at 20°, depending on its insoluble residue content. It is

decomposed slowly by water, but very vigorously by acids, with the evolution of boron hydrides. By treatment with hot HCl, magnesium diboride is completely dissolved, yielding from 0.8 to 1.1% of the total quantity of boron as gaseous boron hydrides. Simultaneously, about 2 moles of hydrogen to 1 mole of MgB_2 (2.11-2.12 moles found experimentally) are evolved, which agrees with the data of Travers and Ray [11]. This provides a basis for assuming the validity of the equation proposed by these authors for the hydrolysis of magnesium boride:

$$MgB_2 + 3H_2O = Mg(OH)_2 + B_2O + 2H_2.$$

Magnesium diboride is a product of the reaction of Mg with boron at relatively low temperatures. Thus, traces of it were observed for the first time by X-ray in mixtures of Mg and B, calcined at 600°. The most favorable temperature for the formation of MgB_2 is about 800°, for which it is desirable to have an excess of Mg in the charge or to use a briquetted charge, because of the high volatility of Mg.

TABLE 3

Results of Experiments on the Distillation of Free Magnesium from Products of Different Composition

Sample	Mg:B ratio present in the charge	Distilled free Mg (% of sample)	Theoretical excess of magnesium (%) from calculation of the composition of the components	Phase composition of the agglomerates
1	1:1	32.4	34.6	MgB_2 + metallic magnesium
2	3:4	25.7	26.5	
3	3:2	52.8	51.5	
4	Boride, according to Stock, obtained from B_2O_3 + Mg	—	—	MgB_2, Mg and MgO
5	1:2	0.0	0.0	MgB_2

At this temperature we can obtain the boride containing no more than 2-5% of insoluble residue which consists of an excess of boron mixed with other insoluble borides.

The maximum temperature for the existence of MgB_2 is below 1050°, since no MgB_2 lines were observed for samples calcined at this temperature.

The data of Table 1 also show that all the products obtained with Mg to B ratios larger than 1:2 yield unaltered MgB_2 and an excess of free magnesium, i.e., that no magnesium boride containing more than 1 atom of magnesium to 2 atoms of boron exists. This is also confirmed by Table 3, in which data are given for the vacuum distillation of the excess of magnesium from the agglomerates obtained at 800°.

TABLE 4

Data on the Composition of Magnesium Diboride Samples

Sample	Insoluble residue (%)	Per cent content		$\frac{\%\,Mg}{\%\,Mg + \%B} \cdot 100$
		Mg	B	
6	1.5	51.5	47.2	52.0
7	5.2	48.8	45.8	51.6
8	6.2	50.6	48.2	53.9
9	6.0	52.6	44.6	54.1

MgB_2 lines were also observed in samples of magnesium synthesized by Stock [6, 7], which were obviously mixtures of magnesium diboride and metallic magnesium.

The chemical composition of the magnesium diboride phase was confirmed by analysis of the purest samples of it (Table 4), if we allow for the possible accuracy of the boron determinations (theoretically, there should be 53.0% Mg and 47.0% B in MgB_2).

The structure of magnesium diboride was determined from powder photographs, and was characterized by the following data: hexagonal system, $\underline{a} = 3.079 \pm 0.001$ kx, $\underline{c} = 3.512 \pm 0.001$ kx, $\underline{c}/\underline{a} = 1.141$ or in angstroms, $\underline{a} = 3.085$ A, $\underline{c} = 3.519$ A (according to the photograph in the VRS chamber with a NaCl standard,), the spatial group $D_{6h}^1 - C^6/mmm$, number of molecules in nucleus $= 1$, $\underline{d}_{X\text{-ray}} = 2.63$ g/cm³. The structure was of the AlB_2 type, and consisted of a trihedral prism of Mg atoms, with a boron atom in the center. The base of the nucleus: Mg (000), $B\left(\frac{1}{3}\frac{2}{3}\frac{1}{2}, \frac{2}{3}\frac{1}{3}\frac{1}{2}\right)$.

The distance between adjacent Mg atoms of a single layer was 3.08 A, the distance between the Mg atoms of adjoining layers was 3.52 A, the Mg–B distance was 2.50 A, and the B–B distance was 1.78 A.

The good agreement of the observed and calculated interplanar distances and line intensities (Table 5) confirmed the validity of the structure found. The results obtained also agreed with the data of other authors [12, 13].

TABLE 5

Experimental and Calculated Interplanar Distances and Line Intensities of the Powder Photographs of MgB_2

hkl	$d/n_{obsd.}$ (in kx)	$d/n_{cald.}$ (in kx)	$I_{obsd.}$	$I_{calc.}$	hkl	$d/n_{obsd.}$ (in kx)	$d/n_{calc.}$ (in kx)	$I_{obsd.}$	$I_{calc.}$
001	3.53	3.512	< 5	8	200	1.334	1.333	5	4
100	2.668	2.667	25	29	201	1.2462	1.2465	20	20
101	2.122	2.124	100	100	003	–	1.1707	0	< 1
002	1.756	1.756	10	13	112	1.1574	1.1577	25	31
110	1.539	1.539	30	24	103	1.0718	1.0719	15	24
102	1.466	1.467	10	10	202	1.0619	1.0619	5	7
111	1.409	1.410	5	3	120	1.0078	1.0079	10	17

Thus, magnesium diboride belongs with the extremely widespread group of the diborides of other metals [14], particularly of the transition metals Zr, Ti, Nb, Ta, V, Cr, Mo, W, which have atomic radii values close to that of magnesium (a ratio of r_B/r_{Me} in the limits of 0.56-0.66). However, we should point out the great chemical activity of MgB_2 in comparison with that of the diborides named, of which only ZrB_2, as is known, also is decomposed by HCl with the evolution of boron hydrides [15], and also in comparison with aluminum diboride, of which an extremely high chemical inertness is characteristic.

TABLE 6

Interplanar Distances and Line Intensities of the Powder Photograph of Phase A

d/n (in kx)	I	d/n (in kx)	I	d/n (in kx)	I	d/n (in kx)	I
4.17	V. wk.*	1.89	Wk.	1.389	Wk.	1.158	Wk.
3.78	Wk.	1.83	Av.	1.343	V. Wk.	1.144	Av.
3.08	Wk.	1.83	Av.	1.321	Str.	1.123	Wk.
2.72	Wk.	1.76	Wk.	1.310	Str.	1.098	Av.
2.52	V. str.	1.71	Wk.	1.300	Wk.	1.081	Av.
2.32	Str.	1.69	Wk.	1.270	Wk.	1.068	Str.
2.26	Av.	1.63	Str.	1.260	Wk.	1.061	Wk.
2.20	Str.	1.60	V. Wk.	1.253	Wk.	1.048	Str.
2.16	Av.	1.58	Wk.	1.219	Wk.	1.045	Wk.
2.05	V. Wk.	1.53	Str.	1.203	V. Wk.	1.026	Str.
2.01	Av.	1.451	Av.	1.166	Av.	1.016	Wk.
1.96	Str.	1.420	Av.				

Insoluble magnesium borides. By X-ray, 3 phases of insoluble magnesium borides were observed which, in contrast to MgB_2, changed neither in composition nor in weight, even on prolonged treatment in HCl. Ordinarily the insoluble borides were obtained in mixtures with other boride phases. Thus, boride A, if it is obtained at a temperature no higher than 1050°, is accompanied by some quantity of MgB_2, boride B is often obtained in mixtures with boride A, and only boride C contains no other boride phase, except for impurities of free boron.

Because of the complexity of the X-ray photographs and the absence of monocrystals of the higher borides, the crystalline structures of these compounds were not elucidated.

Their chemical composition also cannot be established very accurately because of the probable presence in each sample of a certain amount of free, elementary boron, which was analytically impossible to determine separately, and could be identified only hypothetically by X-ray analysis. Nevertheless, the presence of the three specified phases was confirmed by many X-ray analyses both on samples obtained by direct synthesis from the elements at suitable temperatures, and on the thermal decomposition products of both MgB_2 and phase A (Fig. 1 [see plate, page 607]).

The phase A boride. The temperature region for the existence of the phase lies between 900 and 1150°. This phase, after removal of the MgB_2 impurity (solution in HCl), was a dark-cinnamon colored powder with a d^{20} 2.45. The X-ray photograph data for it are presented in Table 6.

The magnesium content in individual samples of this phase, for which lines for elementary boron were observed in a series of X-ray photographs, varied from 19 to 32.5%. The latter circumstance and also the fact that a higher per cent of magnesium was contained in samples obtained from compositions made up for the charges with excess of

* All the abbreviations given are decoded as: V. wk.= very weak, Wk. = weak, Av. = average, Str. = strong, V. str. = very strong.

magnesium B_6 enables us to assume that phase A corresponds in composition to MgB (theoretically there should be 27.2% Mg and 72.8% B). The depressed magnesium content, as compared with the theoretical, in many samples containing this phase, is probably explained by the low thermal stability and the loss of magnesium, as a result of its volatility, which is accompanied by the evolution of an excess of boron in elementary form.

TABLE 7

Experiments on the Synthesis of Boride A

Sample	Mg:B ratio in original mixture	Calcination temperature	Duration of calcination (hours)	Mg content in insoluble portion of the product (%)	Phase composition of product	Remarks
1	Thermal decomposition of MgB_2	1000°	3	32.5		
2	1:4	1000	2.5	24.5	A	Briquetted charge
3	1:4	1050	2	24.0		
4	1:4	1050	2	21.9		
5	1:4	1080	0.5	27.6		
6	1:6	1040	2	18.8	A + elementary boron	
7	1:6	1000	3	19.4		
8	1:4	1060	2	23.1	A	Experiments carried out in a hydrogen atmosphere in graphite test tubes, placed in tightly sealed steel bombs.
9	1:4	1140	3	27.8		
10	1:6	1120	3	24.0		
11	1:6	1030	3	22.3		

On the other hand, the fact that phase A corresponds to the composition MgB_6, and not MgB_4, as Russell, Hirst, Kanda and King [12] wrote, is confirmed, in the first place, by complete analyses of the purest samples of this boride, obtained also for a Mg:B ratio equal to 1:4, and given in Table 8, and in all the experiments carried out with these ratios, we also observed a greater separation of metallic magnesium in comparison with experiments involving a Mg:B ratio of 1:6.

TABLE 8

Analysis of the Purest Samples of Boride Phase A

Sample	Per cent				Total percent of components found
	Mg	B	Si	ΣFe + Al	
8	23.1	73.6	0.2	1.4	98.3
5	27.6	69.4	0.2	0.8	98.0

Furthermore, in special experiments (8-11) carried out in tightly sealed steel bombs, i.e., under conditions preventing the loss of magnesium, the product which was insoluble in HCl contained in all cases a percentage of magnesium, which was either practically equal to, or lower than that corresponding to the formula MgB_6. On the basis of the data cited we may confidently write the formula MgB_6 for phase A.

It should be added that the boride MgB_6 is completely converted to MgB_2 on heating at 800° with an excess of Mg.

The boride, MgB_6, is extremely stable toward dilute HCl [thus, on boiling in HCl (1:1) for 80 hours only 0.019% of B is converted]; it is decomposed slowly by hydrogen peroxide and nitric acid.

Phase B. Phase B gives an X-ray photograph so different from the X-ray photograph of phase A (Table 9) that it is impossible that it pertains to any admixture containing the latter, although the area of its existence was found to be at almost the same temperature limit as that for phase A. The powder containing this phase is of a dark-cinnamon, almost black color and d^{20} 2.47. This phase is obtained at a temperature from 1100 to 1200°, but above 1200° it decomposes with the separation of phase C.

The analysis of the purest samples of this phase, which were not contaminated by phase A, as determined by X-rays, is presented in Table 10.

On the basis of the data obtained, it is as yet difficult to attribute any definite composition to phase B.

Phase C. This high-temperature phase of magnesium borides is extremely stable thermally. It is obvious from the data of Table 2 that it is stable even on prolonged heating in vacuo at 1500°. This indicates the individuality of phase C.

TABLE 9

Interplanar Distances and Line Intensities of the X-ray Photograph of Phase B

d/n (in kx)	I	d/n (in kx)	I	d/n (in kx)	I
7.27	Wk.	2.52	V. wk.	1.68	Wk.
6.43	Av.	2.42	Str.	1.60	Wk.
3.55	Av.	2.32	Av.	1.413	Wk.
3.38	Av.	2.18	Str.	1.284	Wk.
3.22	Wk.	1.78	Wk.	1.234	V. wk.
2.71	Av.	1.75	Wk.	1.224	V. wk.

TABLE 10

Data on the Composition of Boride Phase B

Sample	Method of production	Composition (%)				Total (%)	Phase composition
		Mg	B	Si	Fe + Al		
1	Thermal decomposition of MgB_2 at 1100° for 3 hrs.	19.4	76.0	0.1	0.6	96.1	Phase B
2	Thermal decomposition of MgB_2 at 1150° for 3 hrs.	19.8	76.7	0.5	0.7	97.7	Phase B, well formed
3	Thermal decomposition of MgB_2 at 1200° for 3 hrs.	14.0	80.1	0.4	0.7	95.2	Phase B + lines of phase C
4	Synthesis with a ratio of Mg:B = 1:2 at 1050° for 30 hours.	23.0	—	—	—	—	Phase A + phase B
5	Thermal decomposition of MgB_2 at 1200° for 3 hrs.	19.8	—	—	—	—	Phase B

The powder of this phase also is of a dark-cinnamon color and d^{20} 2.440. The decomposition of this boride occurs with the evolution of elementary boron and with the elimination of metallic magnesium only at a temperature above 1700°.

TABLE 11

Data on the Composition of Boride Phase C

Expt. No.	Conditions of production of the boride	Composition of the boride (%)		Phase composition	Remarks
		Mg	B		
1	Synthesis with a 1:6 ratio at 1200°, 2.5 hours	15.4	82.0	Phase C + indistinct line of boron	Experiment with briquetted charge
2	Thermal decomposition of MgB_6 at 1230° for 1 hour	12.7	82.0	Phase C	
3		14.8	83.5		
4	Thermal decomposition of MgB_6 at 1380° for 1 hour	15.0	81.3		
5	Thermal decomposition at 1300° for 1 hour	13.6	81.6		
6	The same at 1200°	15.0	80.9	Phase C and, perhaps, admixture of elementary boron	
7	" " 1300	15.0	82.2		
8	" " 1400	14.8	81.4		
9	" " 1470	13.8	83.3		
10	" " 1700	0.9	96.6	Pure boron	Experiments in vacuum furnace
11	" " 1900	0.4	97.8		

The boride phase C was produced only at a temperature above 1200°, with any ratio of components, and also by the thermal decomposition of MgB_2 and MgB_6. From the data of Table 8 it is obvious that the composition of this phase corresponds very closely to the formula MgB_{12} (theoretically there should be 15.5% Mg and 84.5% B).

For all samples of this phase, we obtained the same X-ray photographs (Fig. 2 and Table 12), part of the lines being identical to the X-ray photograph of boron, obtained by the discharge reduction of BCl_3 with hydrogen [16, 17]

(i.e., the purest samples of boron), and being completely identical to the X-ray photographs of impure Moissan boron. On some of the X-ray photographs we observed only one superfluous line, obviously due to admixture.

TABLE 12

Interplanar distances and Line Intensities of Phase C

d/n (in kx)	I	d/n (in kx)	I	d/n (in kx)	I
3.88	Wk.	2.16	Wk.	1.48	Wk.
2.82	Av.	2.05	Av.	1.42	Av.
2.60	Av.	1.95	Av.	1.37	Wk.
2.40	Wk.	1.84	Av.	1.34	Av.
2.34	Str.	1.77	Str.	1.30	Wk.
2.24	Av.	1.55	V. wk.	1.27	Wk.

The X-ray data obtained showed that phase C is precisely the difficultly decomposable boride admixture indicated by Moissan [18] in his time. This phase was also observed in the X-ray photograph as a contaminant of purified Moissan boron.

As to the composition of phase C, it is very likely that it corresponds to the formula MgB_{12}, although not exclusively, since part of the boron in this phase is in the elementary form.

Phase C has a strongly expressed chemical stability toward acids. Thus, on boiling with HCl (1:1) for 100 hours, no quantity of Mg and B sufficient for analysis had been converted to the soluble form. Hydrogen peroxide and nitric acid decompose it slowly, even on boiling. The most suitable method for the decomposition of this boride is fusion with carbonates and alkalies.

A probable mechanism of the reduction of boric anhydride by metallic magnesium. The process of obtaining amorphous boron by the Moissan method includes the reduction of a 3-fold excess of boric anhydride by metallic magnesium, preferably in an inert atmosphere. An excess of boric anhydride is used, in the first place, for the purpose of creating a liquid phase to prevent the oxidation of the strongly heated reaction products by the air; in the second place, it is used for the purpose of destroying the stable magnesium borides forming.

From the experiments made for the purpose of obtaining magnesium boride, by the reduction of B_2O_3 with an excess of magnesium, the primary reaction product was MgB_2 (Table 3).

MgB_2 was obtained from the highly exothermic reaction $B_2O_3 + 4Mg \rightarrow MgB_2 + 3MgO$. The exothermicity of this reaction depended not only on the exothermicity of the process of reduction of B_2O_3, but also on the large evolution of heat during the formation of MgB_2 from the elements; therefore, only MgB_2 could be the primary product of the reduction of B_2O_3.

However, since there are only traces of MgB_2 in the products of the reduction of B_2O_3 by magnesium in an excess of boric anhydride, and on the contrary, since the lines of boride phase C (MgB_{12}) were observed for boron obtained after acid treatment, it should be assumed that MgB_2 reacts with an excess of B_2O_3, according to the scheme:

$$2B_2O_3 + 7MgB_2 \rightarrow MgB_{12} + 6MgO + 6B.$$

Actually, "crude" Moissan boron (i.e., subjected to only a brief treatment for dissolving the excess B_2O_3 and MgO), on the basis of literature data [18], and also according to the data from chemical analyses, contains from 8 to 13% Mg, i.e., if one takes the maximum content of Mg as the quantity close to the content of Mg in $MgB_{12} + 6B$ (the right-hand part of the equation). It is evident from the X-ray photograph 6 in Fig. 2 [see plate, page 607] that this corresponds to the fact that the phase composition of "crude" Moissan boron is almost identical to the composition of boride phase C, and contains only elementary boron as an impurity.

The reaction between B_2O_3 and MgB_2 is probably either slightly exothermic, or even endothermic, and therefore preliminary heating of the charge is necessary. The stability of boride phase C toward acids accounts for the generally well-known difficulty of purification of curde boron by acid treatment. Actually, according to a number of literature sources, the production of amorphous boron with a B content above 90-93% is an exceedingly difficult problem [16, 19].

Moissan overcame this obstacle by fusion of the crude boron with a 50-fold quantity of boric anhydride, thus increasing the boron content to 98% by decomposition of the boride.

Naturally, he did not exclude the possibility that during the highly exothermic reduction of B_2O_3 by magnesium there also occurs a successive decomposition of the initially formed lower borides to the higher borides. The brevity of the reaction, however, does not permit us to attribute any substantial role to these processes. According to the data of Stock, the processes can be of known value in the production of magnesium boride, and the optimum $Mg:B_2O_3$ ratio favorable for producing boron hydrides should be chosen, because at too high a reaction temperature the boride is produced, giving a low yield of boron hydrides.

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SUMMARY

1. As a result of the investigation of the system Mg—B, the presence of four boride phases was demonstrated, namely, a hexagonal MgB_2 phase of the AlB_2 structural type, and three other phases, A, B and C, the structures of which have not as yet been established.

2. It was shown that magnesium diboride is an exceedingly active product chemically, and on decomposition with water and acids it yields boron hydrides. The thermal stability of MgB_2 is low, and on heating to high temperatures, it in turn decomposes into boride phases A, B and C with the separation of Mg.

3. We established the temperature limits of the existence of these phases, and also their chemical compositions. In particular, it was shown that the composition of phase A is close to MgB_6, and the composition of phase C is close to MgB_{12}.

4. Boride phase C is characterized by a high chemical and thermal stability, and dissociates only at temperatures above 2000°. This phase was also observed in all the samples of boron Moisson studied.

5. On the basis of the data obtained, preliminary considerations concerning the possible mechanism of the reduction of B_2O_3 by metallic magnesium were expressed.

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REACTIONS OF NITRATES AND NITRITES OF METALS OF THE FIRST AND SECOND GROUPS OF THE D. I. MENDELEEV PERIODIC SYSTEM IN MELTS

XVIII. INVESTIGATION OF THE TERNARY SYSTEM OF LITHIUM, RUBIDIUM AND SILVER NITRATES

P. I. Protsenko and L. M. Kiparenko

The present work contains the results of an experimental investigation of the ternary system of lithium, rubidium and silver nitrates, and is a continuation of the systematic study of the interaction in binary and ternary systems, composed of melts of the nitrates of metals located in the first and second groups of the D. I. Mendeleev table.

In this ternary system we considered the interaction in melts of the nitrates of those metals of the first group, the ions of which have both noble gas electron shells (lithium and rubidium) and base metal electron shells (silver). The ions of the metals indicated differ sharply from one another in their capacity for coordination, which is observed very well from the point of view of polarization concepts. Thus, lithium ion, compared with the ions of the other alkali metals, after beryllium and magnesium, promotes the formation of the largest ionic field strength, equal to 1.7, has a larger electrical affinity — 124, and has the smallest coefficient of polarizability — 0.029 [1, 2].

In the light of the physico-chemical characteristics indicated, rubidium ion shows different properties. The ionic field intensity created by it is less by a factor of more than 3 than that created by lithium, and is equal to 0.5; its coefficient of polarizability is about 50 times larger, and its electrical affinity is considerably smaller, than that of the lithium ion, and they equal 96 and 124, respectively [1, 2].

It is unfortunate that, because of the absence of data in the literature, analogous quantitative characteristics cannot be cited for silver ion.

However, it is known that the energy of formation of this ion, obtained from the energy of ionization and the energy of sublimation, is very large, and that silver ion ranks close to the metals of the platinum group in its capacity for complex formation.

Proceeding from the premises stated, we were interested in considering the ternary combination of the components, and in investigating the mutual effects and chemical actions among them in melts. This is important because in melts, in the absence of water as a solvent, the possibility of hydrate formation is eliminated, and consequently, one of the factors complicating the study of the chemical transformation is removed.

EXPERIMENTAL

Binary systems. 1. The system silver nitrate—rubidium nitrate was studied by A. P. Palkin [3], according to whose data the components of the system form two compounds: $RbNO_3 \cdot AgNO_3$, melting without decomposition at 139.5°, and the compound $2RbNO_3 \cdot AgNO_3$ melting with decomposition at 141°. A duplicate investigation of this system confirmed her general view, but with some differing data. Thus, according to our data, the melting point of the chemical compound $RbNO_3 \cdot AgNO_3$ is 134°, and the decomposition temperature of the chemical compound $2RbNO_3 \cdot AgNO_3$ is 147° (Fig. 1).

2. N. A. Puschin and M. Radoniĉiĉ [4] investigated the structural diagram of the binary system lithium nitrate—rubidium nitrate. The repetition that we carried out confirmed their data. The components of the system formed the chemical compound $LiNO_3 \cdot RbNO_3$, the melting point of which, according to our data, is 193°* (Fig. 1).

3. The structural diagram of the binary system lithium nitrate—silver nitrate was investigated by A. P. Palkin [5], according to whose data the components of the system form a simple eutectic, with no indications of the formation of solid solution; we also confirmed this (Fig. 1).

The ternary system. According to the fusibility diagram of the binary system, one should expect confirmation of the chemical interactions among the components of a ternary system also; it could occur in this way: there would be an intensification or an abatement of the chemical affinity under the influence of a new medium (the third com-

* It was 191° according to the data of N. A. Puschin and M. Radoniĉiĉ.

ponent), and in connection with this, the appearance inside the ternary system of both and area of crystallization of the pure components and an area of crystallization of the chemical compounds – $LiNO_3 \cdot RbNO_3$, $RbNO_3 \cdot AgNO_3$, $2RbNO_3 \cdot AgNO_3$, and also the appearance of polymorphism, inherent in the present case, in the nitrates of silver and rubidium.

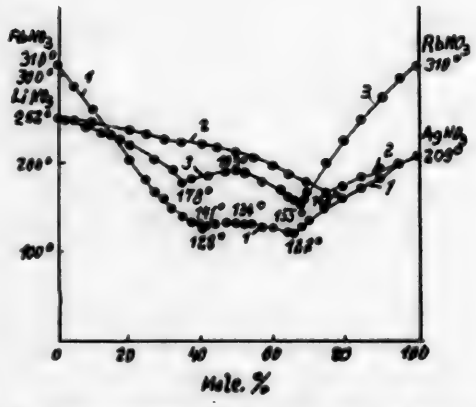

Fig. 1. Binary systems. 1) $RbNO_3$–$AgNO_3$; 2) $LiNO_3$–$AgNO_3$; 3) $LiNO_3$–$RbNO_3$.

The distributions and directions of all fourteen of the sections in the triangle are shown in Fig. 2, and the fusibility curves of these sections are presented in Figs. 3-7. The compositions of the transition points for the ternary sections and the melting points of the mixture of components corresponding to these points, are recorded in the table.

A detailed investigation of the sections enabled us to plot a projection of the isotherms of the three-dimensional structural diagram onto a basic diagram. The isotherms were measured for each 20°, except that in the area of crystallization of the compounds $2RbNO_3 \cdot AgNO_3$ and $RbNO_3 \cdot AgNO_3$ they were measured for each 10°. The isotherms passing through the areas of crystallization of rubidium nitrate were extropolated (Fig. 8), beginning from the 230° isotherm and above.

It is evident from a projection of the liquidus area (Fig. 8) that the ternary system of lithium, rubidium and silver nitrates is a rather complex system. The system is

Note: The letters with the section number show the compositions of the transition points: a – first; b – second; c – third.

Section		Equimolecular percentages			Melting point of transition point
		$LiNO_3$	$AgNO_3$	$RbNO_3$	
I	a	21.75	12.50	65.75	133°
	b	15.00	40.00	45.00	114
	c	11.80	53.00	35.20	106
II	a	29.10	2.50	68.40	148
	b	15.00	50.00	35.00	105
III	a	35.00	35.00	30.00	135
	b	22.50	55.00	22.50	124
IV		23.50	66.50	10.00	149
V	a	55.00	10.00	35.00	158
	b	27.30	5.20	67.50	145
VI	a	45.20	19.80	35.20	146
	b	23.00	10.00	67.00	136
VII	a	32.50	32.50	35.00	133
	b	17.50	17.50	65.00	128
VIII	a	26.00	39.00	35.00	116
	b	17.80	27.20	55.00	122
	c	15.80	24.20	60.00	124
IX	a	19.50	46.00	34.50	104
	b	14.00	34.00	52.00	112
	c	11.00	26.50	62.50	124
X	a	13.00	52.00	35.00	100
	b	9.40	37.60	53.00	114
	c	7.50	30.00	62.50	127
XI	a	7.00	59.00	34.00	113
	b	5.00	41.00	54.00	122
	c	3.75	33.75	62.50	132
XII		14.00	36.00	50.00	113
XIII	a	19.50	45.50	35.00	113
	b	20.00	51.00	29.00	115
XIV		18.40	47.20	34.60	103

characterized by the presence of six areas of crystallization: 1) rubidium nitrate with a crystallization area 12.2% of the total area of the triangle; 2) lithium nitrate 41.7%; 3) silver nitrate 15.2%; 4) chemical compound $LiNO_3 \cdot RbNO_3$ 22.4%; 5) chemical compound $AgNO_3 \cdot 2RbNO_3$ 2.8% and 6) chemical compound $AgNO_3 \cdot RbNO_3$ 5.7%.

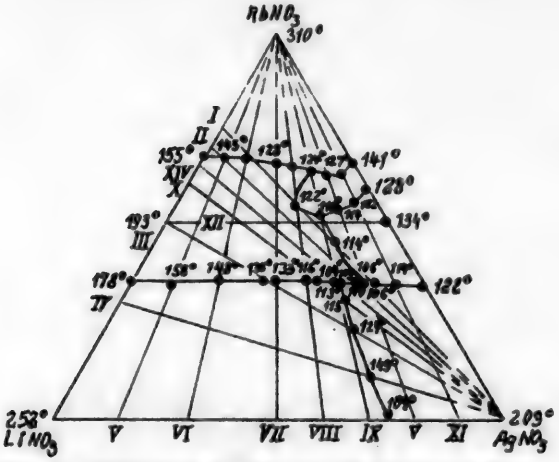

Fig. 2. Distribution and direction of sections in the ternary system.

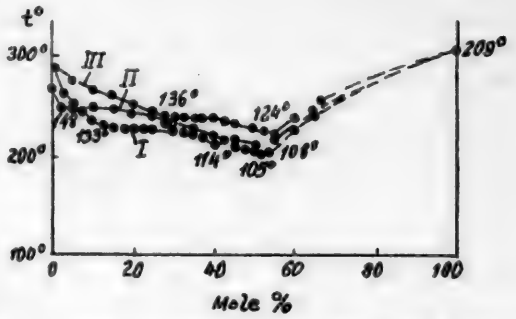

Fig. 3. Internal sections. I) 25% $LiNO_3$ + 75% $RbNO_3$ → → $AgNO_3$; II) 30% $LiNO_3$ + 70% $RbNO_3$ → $AgNO_3$; III) 50% $LiNO_3$ + 50% $RbNO_3$ → $AgNO_3$.

Corresponding to the areas of crystallization of the pure components and of the chemical compounds, there are four non-variant points in the system, three of which are eutectic points and one of which is a transition point.

The first eutectic point corresponds to the composition: 47.4% silver nitrate, 18.6% lithium nitrate, 34% rubidium nitrate and a m.p. of 103°; the second – 53% silver nitrate, 13% lithium nitrate, 34% rubidium nitrate and a m.p. of 100°, and the third – 34% silver nitrate, 14% lithium nitrate, 52% rubidium nitrate and a m.p. of 112°. The transition point corresponds to the composition: 26.5% silver nitrate, 11% lithium nitrate, 62.5% rubidium nitrate and a m.p. of 124° (Fig. 2).

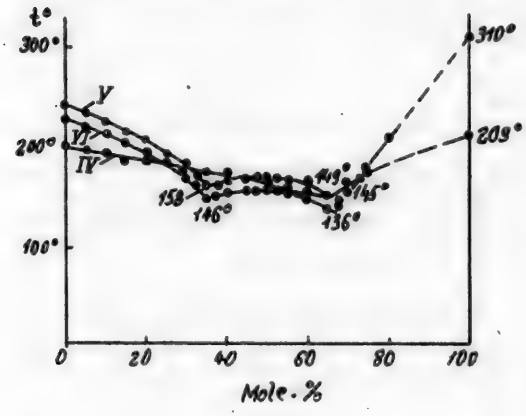

Fig. 4. Internal sections. IV) 30% $LiNO_3$ + 70% $RbNO_3$ → $AgNO_3$; V) 15% $AgNO_3$ + 85% $LiNO_3$ → → $RbNO_3$; VI) 30% $AgNO_3$ + 70% $LiNO_3$ → $RbNO_3$.

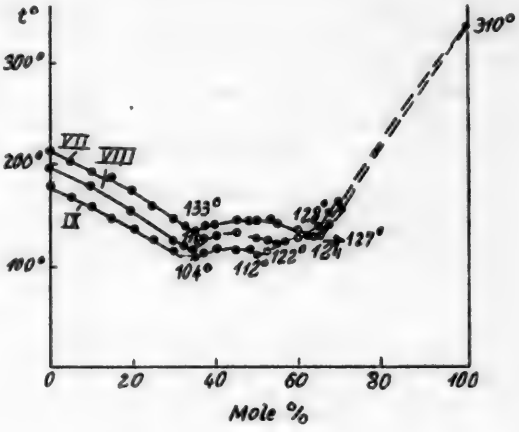

Fig. 5. Internal sections. VII) 50% $LiNO_3$ + 50% $AgNO_3$ → → $RbNO_3$; VIII) 40% $LiNO_3$ + 60% $AgNO_3$ → $RbNO_3$; IX) 30% $LiNO_3$ + 70% $AgNO_3$ → $RbNO_3$.

The orthogonal projection of the path of crystallization onto the lithium nitrate–silver nitrate side is shown in Fig. 9.

The compositions of the three non-variant points were found experimentally and verified by orthogonal projection of the joint crystallization curves.

According to the data of N. A. Puschin [4] and A. P. Rostkovsky [6], rubidium nitrate has several polymorphic transformations. The former author indicated the existence of rubidium polymorphic modifications at 216 and 160.5°. A. P. Rostkovsky found one more polymorphic transformation, the transition point of which was 292°; and he confirmed

the previously known transformations at 166 and 229°. According to A. P. Rostkovsky's treatise, the hexagonal-rhombohedral modification of rubidium nitrate is converted to the normal syngony at 136°, but it is transformed to the anisotropic rhombohedral form on heating to 218.0-219.8°. Both authors secured polymorphic transformations by means of heating and cooling curves. In our investigations of the crystallization branches of rubidium and silver nitrates in binary systems, and also the corresponding sections of any singular point, notwithstanding the evaluation of N. K. Voskresenskaya [7], in our opinion the visual-polythermal method of physico-chemical analysis gives considerably better data for liquidus curves of the salts than does the method of heating and cooling curves. In this investigation, we account for the absence on the rubidium nitrate liquidus curve of discontinuities corresponding to the polymorphic transformation of rubidium nitrate, by the fact that the heat effect of the transformation of one modification of rubidium nitrate to the other is so small that we were unable to detect it, and the crystals of the polymorphic modifications of rubidium nitrate differed so little from each other in external form that we were also unable to separate them visually.

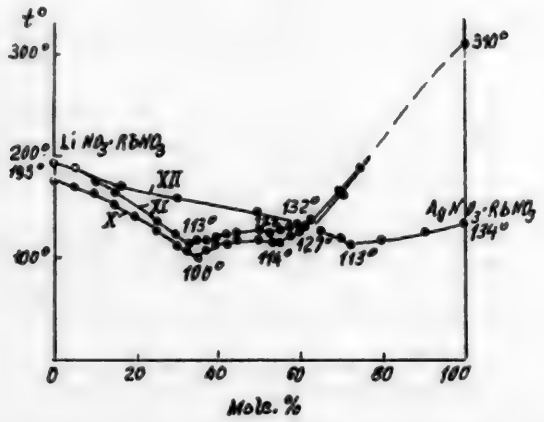

Fig. 6. Internal sections. X) 20% $LiNO_3$ + 80% $AgNO_3$ → $RbNO_3$; XI) 10% $LiNO_3$ + 90% $AgNO_3$ → $RbNO_3$.

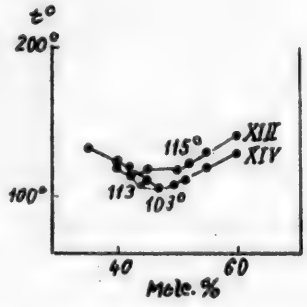

Fig. 7. Internal sections. XIII) 60% $RbNO_3$ + + 40% $LiNO_3$ → $AgNO_3$; XIV) 65% $RbNO_3$ + + 35% $LiNO_3$ → $AgNO_3$.

It was mentioned above that in the investigation of the system of rubidium and silver nitrates we established the chemical compounds $RbNO_3 \cdot AgNO_3$ and $2RbNO_3 \cdot AgNO_3$. The compound $2RbNO_3 \cdot AgNO_3$, which melted with decomposition, and had been difficult to secure in the binary system, rubidium nitrate–silver nitrate, appeared more readily and more clearly in the presence of lithium nitrate as a third component which somewhat changed the reaction conditions by its strong polarizing action. This compound occupied about 3% of the total area of crystallization in the concentration triangle, which indicated an increase of its stability, accounted for by the stabilizing action of lithium nitrate, which depended on the ionic field strength of the latter.

The large area of crystallization of the chemical compound $LiNO_3 \cdot RbNO_3$, which melts without decomposition, surpassing in size the area of crystallization of the pure components of silver and rubidium nitrates, and its melting point differing little from the melting points of the nitrates of silver and rubidium, indicates the stability of

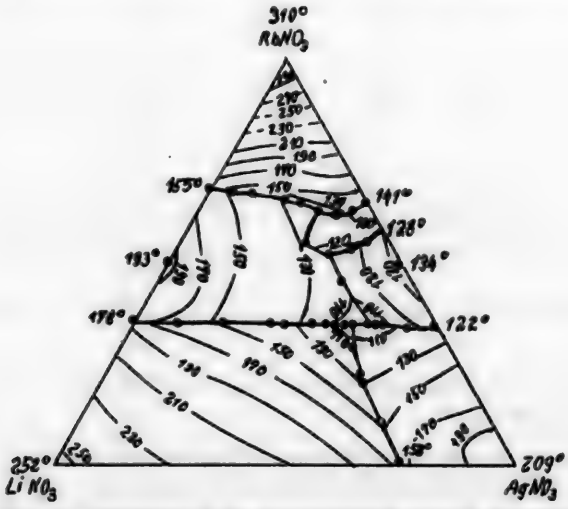

Fig. 8. Projection of the crystallization area of the system onto the basic triangle.

the compound $LiNO_3 \cdot RbNO_3$, which is intensified because of the total polarizing action of lithium and silver ions on rubidium ion at the moment of the formation and crystallization of the compound. Thus, the chemical interaction between the compounds in the binary systems $LiNO_3 | RbNO_3$ and $RbNO_3 | AgNO_3$ which appears clearly in melts, is

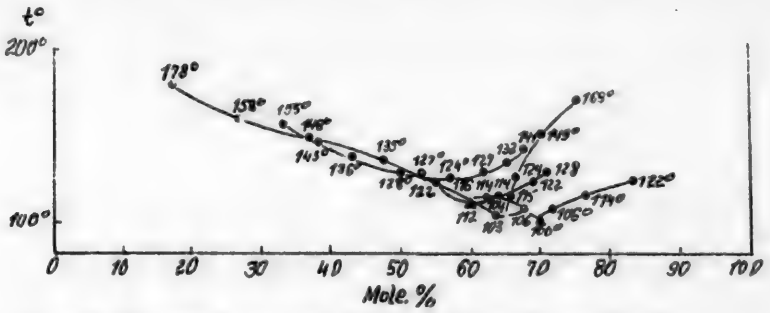

Fig. 9. Orthogonal projection of the joint curve of crystallization onto the $LiNO_3 - AgNO_3$ side.

not weakened in the ternary system of the nitrates of lithium, rubidium and silver, but is intensified under the influence of the total action on rubidium ions of the ionic field strengths of lithium and silver ions.

SUMMARY

1. The ternary system of the nitrates of lithium, rubidium and silver was investigated by the visual-polythermal method of physico-chemical analysis.

2. It was found that the ternary system Li, Rb, $Ag \| NO_3$ behaves as a complex system having four non-variant points, of which three are eutectic points, and the fourth is a transition point.

3. In the melts we verified the formation of the chemical compounds $LiNO_3 \cdot RbNO_3$, $RbNO_3 \cdot AgNO_3$, which melted without decomposition, and the chemical compound $2RbNO_3 \cdot AgNO_3$, which melted with decomposition.

4. It was shown that the chemical interaction in melts of the nitrates of lithium and silver with rubidium nitrate was not weakened in the ternary system, but was intensified under the influence of the mutual overall polarizing action on rubidium ions of lithium and silver ions.

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SINGULAR IRREVERSIBLE-RECIPROCAL SYSTEM WITH SEPARATION OF THE CHLORIDES AND SULFATES OF LITHIUM AND THALLIUM

A. G. Bergman and M. L. Sholokhovich

The chemical interactions taking place in reciprocal systems are demonstrated most clearly by the systematic study of a series of reciprocal systems with a common lateral direction. Of special interest are systems with sharply expressed complex formation, in which it is possible to follow well the relation of the exchange and the complex formation in the lateral direction. At the present time, systematic material in this direction was obtained for a system forming the cationic complexes — $Li_2SO_4 \cdot K_2SO_4$, $Li_2WO_4 \cdot K_2WO_4$ and for the anionic complexes — $BaF_2 \cdot BaCl_2$, $SrF_2 \cdot SrCl_2$, $CaF_2 \cdot CaCl_2$, etc.. In these investigations we showed the extremely great diversity of types of reciprocal systems, particularly, of the adiagonal type, forming in systems with relatively small heats of the exchange reaction in the presence of large heats of complex formation.

The system which we studied was the first of a series of reciprocal systems invblving the participation of the complex $Li_2SO_4 \cdot Tl_2SO_4$, which we investigated for the first time in the present work. This series was of interest because it was more easily fusible than the systems containing the complexes $Li_2SO_4 \cdot K_2SO_4$ and $Li_2WO_4 \cdot K_2WO_4$. We observed that all the thallium salts melted considerably lower than the corresponding potassium salts. The exchange reaction of the system Li, Tl $\|SO_4$, Cl in the Li_2SO_4—Tl_2Cl_2 direction had a heat of 11.83 kcal/equiv.

EXPERIMENTAL

The method of investigation was the visual-polythermal method. The salts were melted in a platinum crucible. The temperature was measured with a Pt—Pt/Rh thermocouple. All the calculations were in equimolecular percentages. The c.p. salts had melting points of: Li_2SO_4 860°, Tl_2SO_4 633°, LiCl 605°, TlCl 429°.

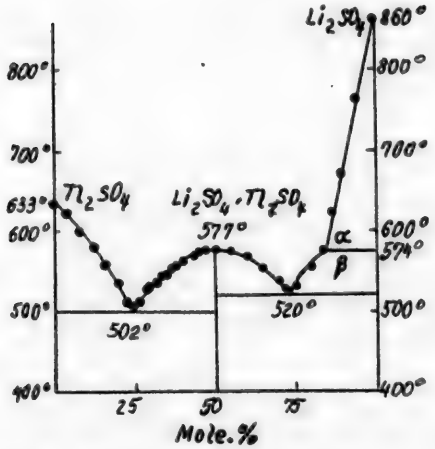

Fig. 1. Binary system Tl_2SO_4—Li_2SO_4.

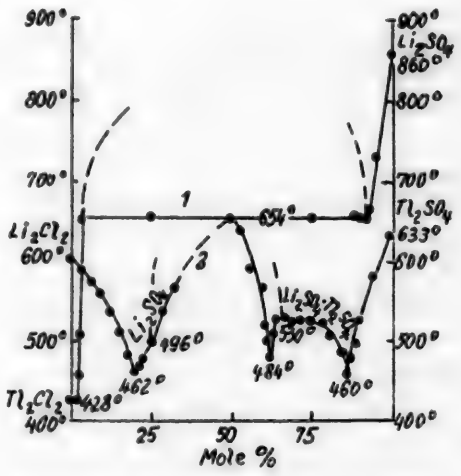

Fig. 2. Diagonal sections of the reciprocal system Li, Tl $\|$Cl, SO_4.

Binary systems. The systems Li_2Cl_2—Si_2SO_4 [1], Li_2Cl_2—Tl_2Cl_2 [2], Tl_2SO_4—Tl_2Cl_2 [3] were eutectic systems.

In the system Tl_2SO_4—Li_2SO_4 (Fig. 1), the compound of the 1:1 composition, which melted at 577° without decomposition, formed. Lithium sulfate exists in two modifications. The transition point of the α-form to the β-form at 574° appears clearly on the Li_2SO_4 curve. The points of intersection of the branches are: 1) 24.5% Li_2SO_4 and 502°, and 2) 73.5% Li_2SO_4 and 520°.

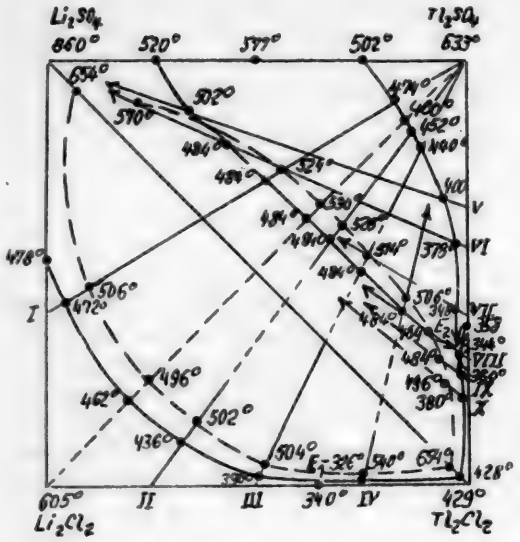

Fig. 3. Scheme of internal sections in the system.

Diagonal system. 1. [illegible] Tl_2Cl_2–Li_2SO_4 (Fig. 2) was stable, and was characterized by a limited mutual solubility of the components in the liquid state. The interval of separation was from 4 to 92.5% lithium sulfate. The three phase monotectic process proceeds within this interval. The eutectic point was at 2% Li_2SO_4 and 428°. 2. The Li_2Cl_2–Tl_2SO_4 (Fig. 2) section intersects all areas of crystallization of the reciprocal system. The interval of separation is from 25% Tl_2SO_4 and 496°, to 65% Tl_2SO_4 and 530°.

Unlike the stable section, in the present section the separation of the solid phase of the areas of separation proceeds at a variable temperature, since a univariant equilibrium occurs. The points of intersection of the branches are: 1) 20.5% Tl_2SO_4 and 462°, 2) 62.5% Tl_2SO_4 and 484°, and 3) 89% Tl_2SO_4 and 460°.

The Reciprocal System

We investigated 10 internal sections (Tables 1 and 2, Figs. 4a, 4b and 5). Their arrangement is shown in Fig. 3. The plane of crystallization of the reciprocal system (Figs. 6-9)* consists of five areas. The distribution of the planes of the composition square among the areas of crystallization is presented in Table 3.

TABLE 1

Specific Points of the Internal Sections in the Tl_2SO_4 Direction

Section	Composition of initial mixture	Intersection points of crystallization branches of different phases				Interval of separation			
						from		to	
		point	name of branches	Tl_2SO_4 (mole %)	temperature	Tl_2SO_4 (mole %)	temperature	Tl_2SO_4 (mole %)	temperature
I	[40% Li_2SO_4 + 60% Li_2Cl_2]	1	LiCl and Li_2SO_4	5.0	472°	10.0	506°	56	524°
		2	Li_2SO_4 and compound	52.5	484				
		3	Compound and Tl_2SO_4	82.5	474				
II	[75% Li_2Cl_2 + 25% Tl_2Cl_2]	1	LiCl and Li_2SO_4	10.0	436	15.5	502	60.0	528
		2	Li_2SO_4 and compound	57.0	484				
		3	Compound and Tl_2SO_4	82.5	452				
III	[50% Li_2Cl_2 + 50% Tl_2Cl_2]	1	LiCl and Li_2SO_4	2.5	390	5.0	504	52.5	514
		2	Li_2SO_4 and compound	50.0	484				
		3	Compound and Tl_2SO_4	78.5	440				
IV	[25% Li_2Cl_2 + 75% Tl_2Cl_2]	1	TlCl and Li_2SO_4	1.0	354	2.5	540	43.0	506
		2	Li_2SO_4 and compound	40.0	484				

A lens of separation occupying 51.7% of the surface of the system was located along the stable diagonal of the profile of the reciprocal system. The area of separation was superimposed on two areas – on a major part of the lithium sulfate area and on a small part of the area of the double sulfate of lithium and thallium. The line of joint crystallization of the salts indicated is a straight line and passes through the region of separation, through which the four-phase monotectic process passes.

From the scheme of the crystallization branches of the system (Fig. 8), and from the projection of the crystallization branches of the reciprocal system onto the Li_2SO_4–Li_2Cl_2 side (Fig. 7), it follows that there are three triple non-variant points (Table 4) in the system.

The binary eutectic point of 428° of the diagonal section, Tl_2Cl_2–Li_2SO_4, appears to be a stable triangulation profile of the system.

* See plate p. 607.

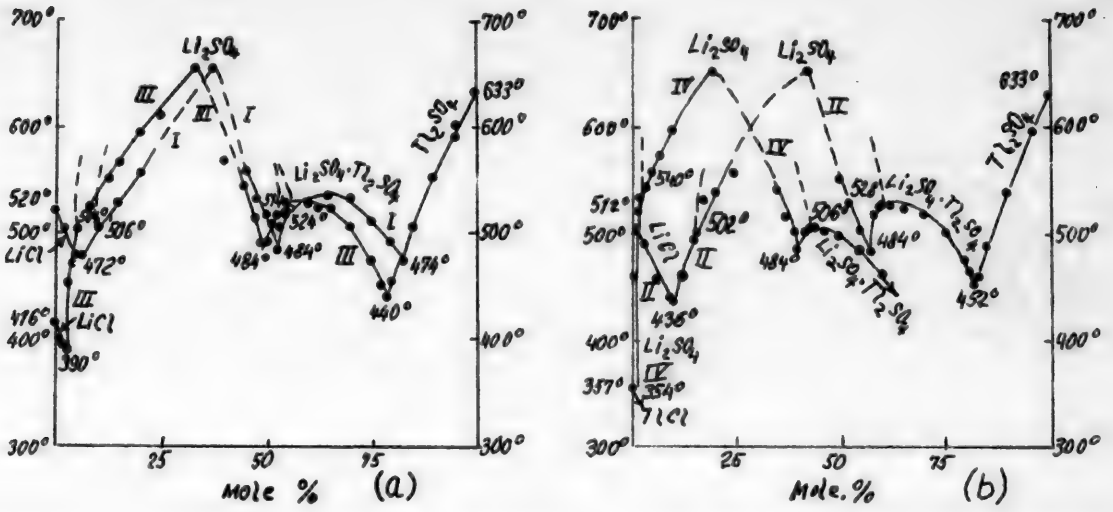

Fig. 4. Internal sections. a: I) 40% Li_2SO_4 + 60% $LiCl_2$ → Tl_2SO_4; III) 50% Li_2Cl_2 + 50% Tl_2Cl_2 → Tl_2SO_4; b: II) 75% Li_2Cl_2 + 25% Tl_2Cl_2 → Tl_2SO_4; IV) 25% Li_2Cl_2 + 75% Tl_2Cl_2 → Tl_2SO_4.

The second triangulation profile $Li_2SO_4 \cdot Tl_2SO_4 - Tl_2Cl_2$ was not stable, since Li_2SO_4 separates inside the system as a result of the cleavage of the complex $Li_2SO_4 \cdot Tl_2SO_4$, by which the system $Li_2SO_4 - Tl_2Cl_2 - Tl_2SO_4$, in turn undergoes triangulation into two phase triangles. Both triple non-variant points of the triangle indicated are located almost in a line in one phase triangle, $Li_2SO_4 \cdot Tl_2SO_4 - Tl_2SO_4 - Tl_2Cl_2$. Consequently, one of them is a eutectic point at 330°, and the other is a transition point at 338°. Thus, the double compound $Li_2SO_4 \cdot Tl_2SO_4$, melting without decomposition inside the reciprocal system, becomes one melting with decomposition.

TABLE 2

Specific Points of the Internal Sections in the Li_2SO_4 Direction

Section	Composition of initial mixture	Intersection points of crystallization branches of different phases				Interval of separation			
						from		to	
		point	name of branches	Li_2SO_4 (mole %)	temperature	Li_2SO_4 (mole %)	temperature	Li_2SO_4 (mole %)	temperature
V	[65% Tl_2SO_4 + + 35% Tl_2Cl_2]	1	Tl_2SO_4 and compound	5.5	400°	Does not pass through region of separation			
		2	Compound and Li_2SO_4	66.0	502				
VI	[55% Tl_2SO_4 +	1	Tl_2SO_4 and compound	3.0	378	48.0	524°	79.0	570°
	+ 45% Tl_2Cl_2]	2	Compound and Li_2SO_4	56.0	484	–	–	–	–
VII	[40% Tl_2SO_4 +	1	Tl_2SO_4 and compound	2.5	348	23.0	514	Not determined	
	+ 60% Tl_2Cl_2]								
VIII	[30% Tl_2SO_4 +	1	TlCl and Li_2SO_4	2.0	344	9.0	497	Not determined	
	+ 70% Tl_2Cl_2]	2	Compound and Li_2SO_4	15.5	484	–	–	–	
IX	[25% Tl_2SO_4 +	1	TlCl and Li_2SO_4	1.0	360	6.0	484	Not determined	
	+ 75% Tl_2Cl_2]								
X	[20% Tl_2SO_4 +	1	TlCl and Li_2SO_4	1.0	380	5.0	496	Not determined	
	+ 80% Tl_2Cl_2]								

Thus, in spite of the presence in the system of the distinctly expressed double compound, $Li_2SO_4 \cdot Tl_2SO_4$, the system undergoes a triangulation of the diagonal type; apparently, in the present case the heat of the exchange reaction prevails over that of complex formation.

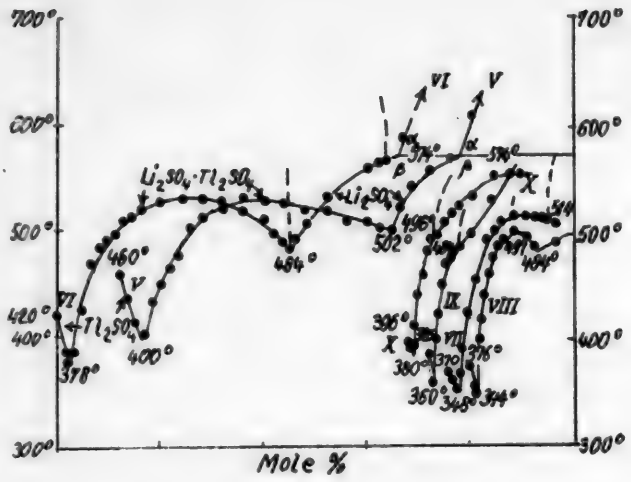

Fig. 5. Internal sections. V) 65% Tl_2SO_4 + 35% Tl_2Cl_2 → Li_2SO_4; VI) 55% Tl_2SO_4 + 45% Tl_2Cl_2 → Li_2SO_4; VII) 40% Tl_2SO_4 + 60% Tl_2Cl_2 → Li_2SO_4; VIII) 30% Tl_2SO_4 + 70% Tl_2Cl_2 → Li_2SO_4; IX) 25% Tl_2SO_4 + 75% Tl_2Cl_2 → Li_2SO_4; X) 20% Tl_2SO_4 + 80% Tl_2Cl_2.

TABLE 3

Area	Areas of crystallization	Area (%)
1	Lithium chloride	10.0
2	Thallium chloride	1.3
3	Thallium sulfate	5.3
4	Double sulfate of lithium and thallium	22.8
5	α-Modification of lithium sulfate	2.0
6	β-Modification of lithium sulfate	58.6

It is extremely interesting that the complex $Li_2SO_4 \cdot Tl_2SO_4$ corresponded to a sharply expressed crest on the diagram, although it deviated appreciably from the plane of the present section.

DISCUSSION OF RESULTS

As to the high value of the conventionally calculated heat of the exchange reaction, equal to 11.83 kcal/equiv., in spite of the presence of sharply expressed complex formation, the system triangulated according to the diagonal type and seemed to be of the nature of an irreversible reciprocal system of the singular type with separation. The stably triangulating section is the Li_2SO_4–Tl_2SO_4 diagonal. The double sulfate area, although it also exists in the system at the lowest temperature is, however, transformed within the reciprocal system to a compound which melts with decomposition, as a result of which free lithium sulfate separates as the primary phase on the profile. The present system seems to be one of the few examples of systems in which a sharply expressed complex formation is related to the separation of the components of the stable pair.

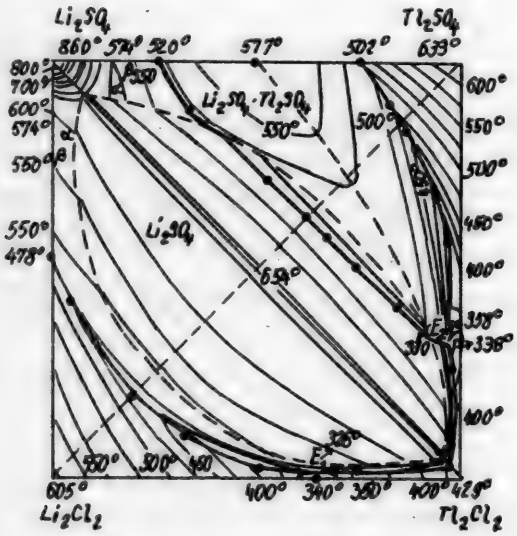

Fig. 6. Projection of the three-dimensional diagram of the system onto a composition square.

The region of separation consisted of 51.7% of the area of the liquidus plane of the system and, located between 4 and 92.5% lithium sulfate along the diagonal, was superimposed on a major part of the lithium sulfate area, and also on a small part of the double sulfate area.

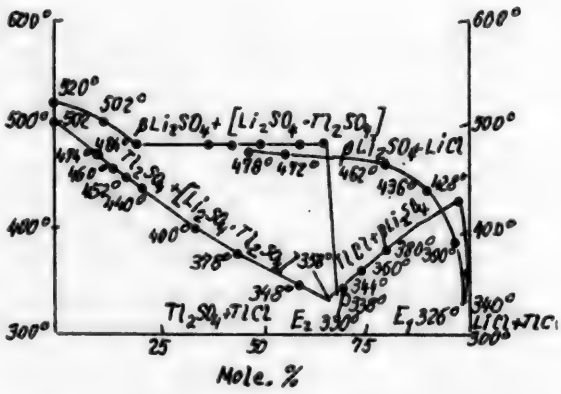

Fig. 7. Projection of the crystallization branches of the system onto the Li_2SO_4–Li_2Cl_2 side.

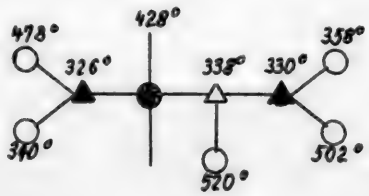

Fig. 8. Scheme of crystallization branches of the system Li, Tl ‖ Cl, SO_4.

TABLE 4

Characteristics and Composition of the Non-Variant Points

Designation of point and its character	Temperature	Composition				Equilibrium phases
		Tl_2Cl_2	Li_2Cl_2	Li_2SO_4	Tl_2SO_4	
Eutectic E_1	326°	65	34	1	—	LiCl, TlCl, Li_2SO_4
Transition P	338	68	—	2	30	TlCl, Li_2SO_4, $Li_2SO_4 \cdot Tl_2SO_4$
Eutectic E_2	330	66	—	3	31	TlCl, Tl_2SO_4, $Li_2SO_4 \cdot Tl_2SO_4$

The line of joint crystallization of the salts passed through the region of separation and was a straight line along which passed the four-phase monotectic process. The asymmetry of the lens of separation, which apparently brings about the formation of the complex, $Li_2SO_4 \cdot Tl_2SO_4$ is of great interest. We turn our attention to the fact that the isotherms in the area of $Li_2SO_4 \cdot Tl_2SO_4$ complex acquire a singular character on reduction of the temperature, and therefore, the peak on the crystallization plane of this complex is semi-singular.

SUMMARY

1. The plane of crystallization of the system consisted of five areas.

2. The diagonal section Li_2SO_4—Tl_2Cl_2 in the system was a stable section, but the adiagonal profile $Li_2SO_4 \cdot Tl_2SO_4$—Tl_2Cl_2 was not stable.

3. The sharply expressed double compound $Li_2SO_4 \cdot Tl_2SO_4$ which melted without decomposition, was transformed within the reciprocal system to a compound which melted with decomposition.

4. Separation took place in the system. The lens of separation was located along the stable diagonal, and occupied 51.7% of the area of the system, between 4 and 92.59% Li_2SO_4 on the diagonal.

5. The region of separation was superimposed on two areas — on the Li_2SO_4 area and on the area of the compound $Li_2SO_4 \cdot Tl_2SO_4$.

6. An asymmetry of the lens of separation occurred under the influence of sharply expressed complex formation.

7. The peak in the area of crystallization of the complex $Li_2SO_4 \cdot Tl_2SO_4$ became semi-singular on reduction of the temperature.

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IRREVERSIBLE-RECIPROCAL SYSTEM OF THE CHLORIDES AND SULFATES OF LITHIUM AND STRONTIUM

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The interaction of salts in melts depends on a number of factors, first among which are the charges, radii and electron structures constituting the ions of these salts.

A consideration of the structural diagram from the point of view of the positions in the D. I. Mendeleev table of the elements constituting the system, enables us to detect the effect of the sizes of the charges and the radii, and the effect of the structure of the electron shell of one ion or another on the character of the system. Ions which are closely related in the properties listed should form similar systems in analogous combinations with the rest of the ions.

A graphic example of such a similarity might be the reciprocal system Li, Ca ‖ Cl, SO_4 [1] which was studied earlier, and introduced into the present work as Li, Sr ‖ Cl, SO_4.

TABLE 1

Areas of Sections of Crystallization of the System Li, Sr ‖ Cl, SO_4

Section of crystallization	Area occupied (%)
$SrSO_4$	78.7
LiCl	13.0
$SrCl_2$	5.3
Li_2SO_4	3.0

EXPERIMENTAL*

The system was studied by the visual-polythermal method of fusibility in a platinum crucible in an electric shaft furnace. We measured the temperature with a Au, Pd, Pt—Pt, Rh thermocouple. All compositions were expressed in equimolecular percentages. As the starting materials, we used the pure salts: LiCl, 609°; Li_2SO_4, 852°; and $SrCl_2$, 873°.

According to the data in the literature [2] the conventional melting point of $SrSO_4$ is 1605°.

TABLE 2

Composite Table of Internal Sections of the System

Section	Initial mixture of components	M.p. of initial composition	Added component	Branches of crystallization curves and their intersections						
				branch 1	intersection A**	intersection t°	branch 2	intersection A**	intersection t°	branch 3
I	25% $SrCl_2$ + 75% Li_2Cl_2	550	$SrSO_4$	Li_2Cl_2	13.5	512	$SrSO_4$			
II	25% Li_2SO_4 + 75% Li_2Cl_2	560	$SrSO_4$	Li_2Cl_2	14.5	496	$SrSO_4$			
III	95% $SrCl_2$ + 5% $SrSO_4$	841	Li_2SO_4	$SrCl_2$	8	708	$SrSO_4$	92	661	Li_2SO_4
IV	75% $SrCl_2$ + 25% Li_2Cl_2	657	Li_2SO_4	$SrCl_2$	8	520	$SrSO_4$	91	632	Li_2SO_4
V	55% $SrCl_2$ + 45% Li_2Cl_2	529	Li_2SO_4	$SrCl_2$	6.5	460	$SrSO_4$	88.5	612	Li_2SO_4
VI	65% Li_2SO_4 + 35% Li_2Cl_2	528	$SrSO_4$	Li_2SO_4	4	490	$SrSO_4$			
VII	25% Li_2Cl_2 + 75% Li_2SO_4	566	$SrSO_4$	Li_2SO_4	5	562	$SrSO_4$			
VIII	40% Li_2SO_4 + 60% Li_2Cl_2	520	$SrSO_4$	Li_2Cl_2	9.5	482	$SrSO_4$			
IX	65% Li_2Cl_2 + 35% $SrCl_2$	532	$SrSO_4$	Li_2Cl_2	8.7	488	$SrSO_4$			
X	45% Li_2SO_4 + 55% Li_2Cl_2	508	$SrSO_4$	Li_2Cl_2	8.5	477	$SrSO_4$			

Binary systems. (Fig. 1). The systems 1) Li_2Cl_2—Li_2SO_4 [3, 4], 2) Li_2Cl_2—$SrCl_2$ [5], and 3) Li_2SO_4—$SrSO_4$ [6] were studied earlier; 4) we studied $SrCl_2$—$SrSO_4$ for the first time. All four systems were simple eutectic systems. According to our data the eutectics were located as follows: in the first system it was at 485° and 48.7% Li_2Cl_2, in the second —at 488°, and 51.2% Li_2Cl_2, in the third —at 722° and 22% $SrSO_4$, and in the fourth —at 762° and 14% $SrSO_4$. On the

* With the cooperation of T. T. Logachev.

** A is the equimolecular per cent of added component.

Li_2SO_4 crystallization branch in the system Li_2Cl_2—Li_2SO_4 at 572° there is a discontinuity corresponding to a heteromorphic transition.

In all cases a homeomorphic transition was reflected at 564° on the LiCl branch.

Diagonal profiles (Fig. 1). We repeated the diagonal profiles studied earlier [6]. The conventional heat of the exchange reaction of Li; Sr ‖ Cl, So_4 is 0.47 kcal/g-equiv. in the direction of the Li_2SO_4—$SrCl_2$ pair. However,

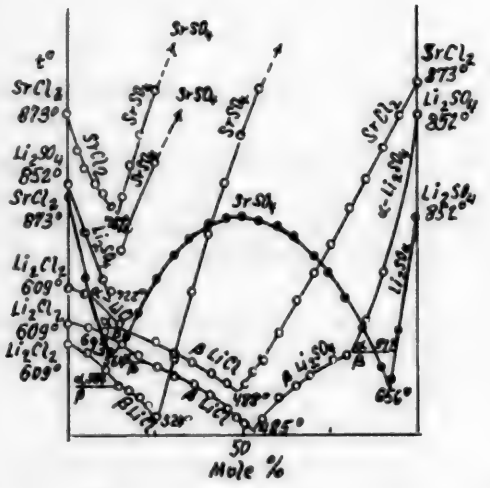

Fig. 1. Secondary directions and diagonal sections of the reciprocal system Li, Sr ‖ Cl, SO_4.

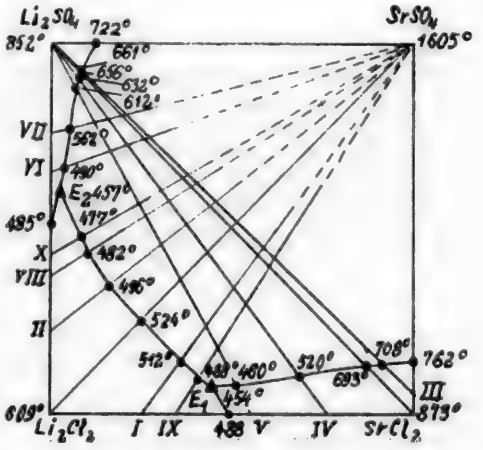

Fig. 2. Distribution of internal sections in the reciprocal system Li, Sr ‖ Cl, SO_4.

the stable diagonal section in this system is another diagonal Li_2Cl_2—$SrSO_4$ with a eutectic at 524° and 25% $SrSO_4$. The $SrCl_2$ — Li_2SO_4 diagonal intersects both the component areas and the area of the exchange product of $SrSO_4$, at 693° and 12%, and 656° and 92%, respectively.

Internal sections (Fig. 3). The crystallization area of the system was studied by 10 internal sections; their distribution is given in Fig. 2. The fundamental data for each section were arranged in a composite table.

A projection of the crystallization area of the three-dimensional diagram onto a composition square (Fig. 4) indicated the existence in the system of four areas of crystallization of its components. We made a triangulation of the system, obtaining two phase triangles for the stable diagonal of section Li_2Cl_2—$SrSO_4$.

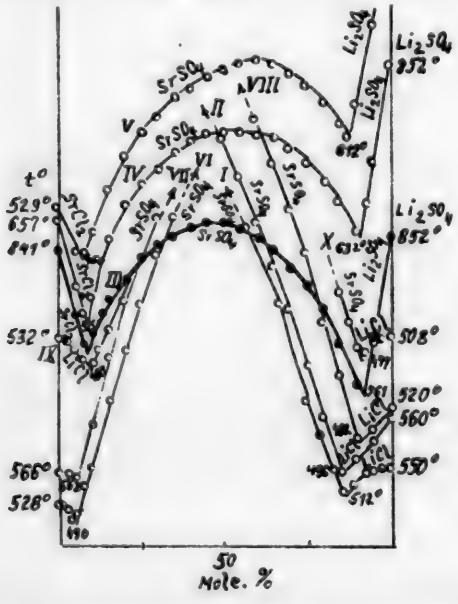

Fig. 3. Internal sections in the reciprocal system Li , Sr ‖ Cl, SO_4.

A projection of the joint crystallization curve onto the side of the composition square (Fig. 5) showed a regular decrease of temperature for these curves, and showed their convergence at two of the three eutectic points (E_1 and E_2).

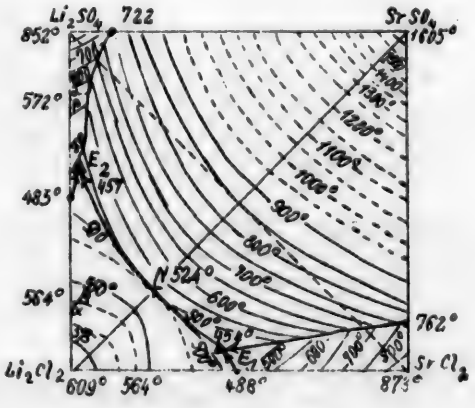

Fig. 4. Projection of the three-dimensional diagram of the reciprocal system Li, Sr ‖ Cl, SO_4 onto the composition square.

In the $SrSO_4$ area the isotherms form a well-expressed peak, which inclines somewhat toward the Li_2SO_4 side from the plane of the stable diagonal, and which indicates the tendency toward exchange reactions between the components of the stable pair.

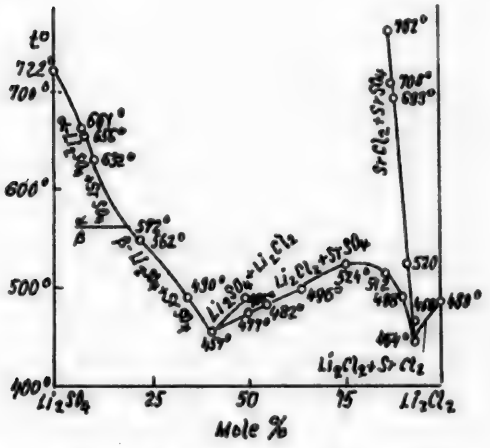

Fig. 5. Projection of the joint lines of crystallization of the system Li, Sr ||Cl, SO_4 onto the Li_2SO_4–Li_2Cl_2 side.

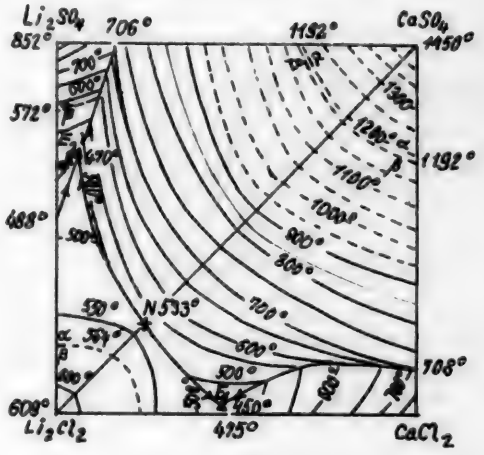

Fig. 6. Projection of the three-dimensional diagram of the reciprocal system Li, Ca ||Cl, SO_4 onto the composition square.

The maximum area of crystallization equal to 78.7% (Table 1), corresponds to the most difficultly fusible component, $SrSO_4$.

A comparison of the structural diagrams of the two reciprocal systems Li, Ca ||Cl, SO_4 (Fig. 6) and Li, Sr ||Cl, SO_4 (Fig. 4) showed their very great similarity, which included the very similar forms of all the areas of crystallization, the close values of the sizes of the areas that they occupied, and the location of the isotherms and multiple points.

It is possible to account for the observed similarities by the rather close values of the ionic radii of Ca^{++} – 1.06 A and Sr – 1.27 A, which have the same charge and an analogous 8-electron structure for the outer electron layer.

SUMMARY

1. The reciprocal system Li, Sr ||Cl, SO_4, studied by the visual-polythermal method of fusibility, belongs to the irreversible-reciprocal systems which show no complex formation.

2. A discrepancy was found between the value of the thermal effect of the exchange reaction (0.47 kcal/g-equiv.) and the character of the diagram of the reciprocal system; judging from the value of the thermal effect, the system should be reversible-reciprocal [7], which does not agree with experiment.

3. A discrepancy was found between the thermal effect and the direction of displacement of the exchange reaction in the system. In conformity with the thermal effect, the exchange reaction should be displaced toward the side of the pair $SrCl_2$–Li_2SO_4, whereas in reality it takes the opposite direction.

4. The great similarity found in the nature of the structural diagrams of the systems Li, Ca ||Cl, SO_4 and Li, Sr ||Cl, SO_4 is explained by the close values of the sizes of the ionic radii of calcium and strontium ions, which have an identical charge and a similar structure for the outer electron layers.

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ELECTROCHEMICAL INVESTIGATION OF SOME BINARY SYSTEMS IN NITROMETHANE

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Solutions of aluminum and antimony halides and their complexes in nitro derivatives of hydrocarbons have interesting electrochemical properties. Such solutions were studied in greatest detail in nitrobenzene, in an investigation in which Plotnikov and his coworkers were engaged. A solution of aluminum bromide in nitrobenzene is a good conductor and as shown by Plotnikov [1], and later by Plotnikov and Bendetsky [2], its specific electrical conductivity passes through a maximum.

It was found that nitrobenzene solutions of aluminum bromide and aluminum chloride have the power to dissolve the alkali metal halides, which do not dissolve in nitrobenzene by themselves.

It is interesting to note that during electrolysis of these ternary systems the alkali metal is deposited at the cathode, whereas during electrolysis of the benzene and toluene solutions of these same complexes, aluminum is deposited at the cathode. Here the specific effect of the solvent on the process of electrolytic dissociation appears. It is obvious that the process of complex formation underlies this.

An electrochemical investigation of solutions of the antimony halides and their complexes in nitrobenzene was made by Vaisberg [3]. In much less detail he investigated solutions of aluminum and antimony halides in nitromethane. In general the small number of inorganic salts soluble in nitromethane should be noted, about which there is an indication by Brunner [4]. A small number of works on the electrical conductivity of solutions of inorganic salts in nitromethane was cited in Walden's [5] monograph. Solutions of aluminum bromide and some of its complexes in nitromethane were studied by Mezhennyi [6]. He studied the binary system, $AlBr_3$—nitromethane, and of the ternary systems, $AlBr_3$—$LiCl$—CH_3NO_2 and $AlBr_3$—KCl—CH_3NO_2, were studied. It was found that, during the electrolysis of these ternary systems, alkali metal deposits at the cathode. We also studied the binary systems $AlBr_3$—$NaCl$, $AlBr_3$—KBr, $AlCl_3$—$NaCl$, $SbBr_3$—KBr, in this solvent, for the purpose of broadening our knowledge of the nitromethane solutions.

EXPERIMENTAL

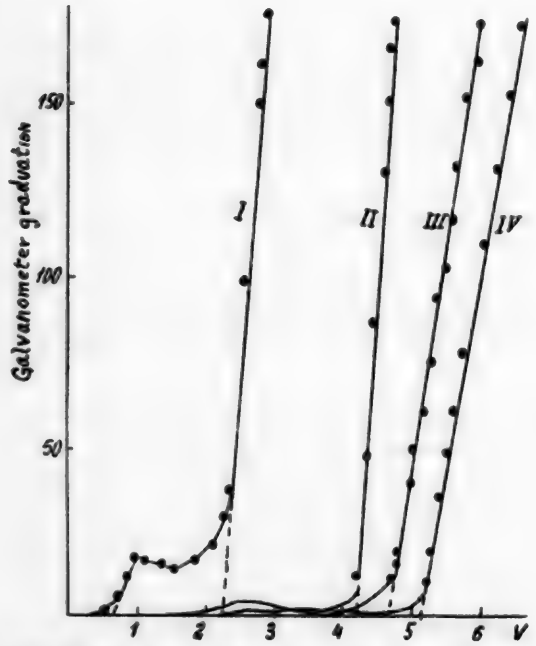
Nitromethane was synthesized from chloroacetic acid and sodium nitrite. The resulting product was distilled, dried with fused calcium chloride, then the nitromethane was distilled over mercuric oxide. The final product was distilled directly into an ampoule and sealed up. The specific electrical conductivity of the nitromethane at 20° was $5.3 \cdot 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

Chemically pure anhydrous preparations of the salts were used for the investigation. A vessel with a ground-glass stopper and platinized platinum electrodes was used for the measurements of the electrical conductivity. The electrical conductivity was measured in a water thermostat at 20° by means of a tube oscillator. The solutions were prepared in the following way. Into a previously weighed vessel for measurement of the electrical conductivity, we poured a certain quantity of fused aluminum bromide from an ampoule. After cooling, the vessel was weighed, the nitromethane was added, and it was reweighed. The electrical conductivity of the initial solution was determined, and then a constantly increasing quantity of alkali metal halide was added. After each addition, the electrical conductivity was measured. Thus, at a constant ratio of aluminum bromide and nitromethane, solutions with different ratios of aluminum bromide and alkali metal halide were obtained.

Similar experiments were also carried out with other ternary systems containing aluminum chloride and antimony bromide. An evolution of heat was observed during the dissolving of $AlBr_3$ and $AlCl_3$ in nitromethane. The electrical conductivity of the solutions of the aluminum and antimony halides in nitromethane increased (Tables 1, 2, 3, 4, 5) on addition of the alkali metal halides.

The alkali metal halides ceased to dissolve as the ratio between them and the Al and Sb halides approached unity. Since the increase of the electrical conductivity was related to the dissolving of the alkali metal salts, it is natural that, as the ratio between the alkali metal halides and the aluminum and antimony salts approached unity, the electrical conductivity ceased to increase. A study was made of the system, $AlBr_3$—$NaCl$—nitromethane, for two ratios of $AlBr_3$:nitromethane. It is obvious that the solution with the larger $AlBr_3$ content had the higher electrical conductivity, although the forms of the curves for both were identical. There is a similar type of curve for the three remaining systems.

The increase of the electrical conductivity on addition of alkali metal halides, and the fact that the dissolving ceased when the ratio between the alkali metal halides and the aluminum or antimony halides approached unity, enabled us to assume that in the solutions complexes are formed which contain one molecule of alkali metal halide, of such compositions as: $NaCl \cdot AlCl_3$, $NaCl \cdot AlBr_3$, $KBr \cdot AlBr_3$ and $SbBr_3 \cdot KBr$. We did not exclude the possibility that molecules of solvent enter into the composition of a complex.



Decomposition voltage of nitromethane solutions. I) $SbBr_3$—KBr; II) $AlCl_3$—NaCl; III) $AlBr_3$—NaCl; IV) $AlBr_3$—KBr.

The solutions of $AlBr_3$—NaCl and $AlBr_3$—KBr thickened during storage, and after several days they were transformed to gels. At first these gels were transparent, straw-yellow colored masses, which after several days were converted to opaque white gels. After a series of measurements was made, the solution was not poured from the vessel used for measuring the electrical conductivity, but remained in it, where from time to time the electrical conductivity was checked. It was found that the electrical conductivity of the ternary systems had not changed during 7-10 days, and only after this did it begin to decrease.

Solutions of $AlCl_3$—NaCl and $SbBr_3$—KBr did not gel completely on storage. Thus, experiments showed that gelation was characteristic only for solutions containing aluminum bromide. Experiments were also carried out on solutions of $AlBr_3$ in nitromethane without the addition of alkali metal salts. Our experiments confirmed Mezhennyi's observation that solutions of $AlBr_3$ in nitromethane gel. Simultaneously, we observed a phenomenon not described in the work of Mezhennyi, namely – it was found that the electrical conductivity of solutions of $AlBr_3$ in nitromethane decreases strongly with time, and it decreased more rapidly in the more concentrated solutions. It is possible to assume here that gel formation is related to the continuous process of chemical reaction of aluminum bromide with the solvent. The fact that the electrical conductivity remains constant in the ternary systems over a long period of time is an additional indication that the alkali metal halides bind $AlBr_3$ into complexes, and therefore, the activity of its interaction with the solvent diminishes.

TABLE 1

Change of the Specific Electrical Conductivity of the System $AlBr_3$—NaCl—Nitromethane with a Change of the Ratio $\frac{NaCl}{AlBr_3}$. $AlBr_3$: nitromethane = 1:8.64.

Molecular ratio $\frac{NaCl}{AlBr_3}$	0	0.169	0.355	0.506	0.727	0.95	1.2
$\kappa \cdot 10^3\ \Omega^{-1}\ cm^{-1}$	16.85	20.1	25.5	30.0	36.0	41.5	42

TABLE 2

Change of the Specific Electrical Conductivity of the System $AlBr_3$—NaCl—Nitromethane with a Change of the Ratio $\frac{NaCl}{AlBr_3}$. $AlBr_3$: nitromethane = 1:80.13

Molecular ratio $\frac{NaCl}{AlBr_3}$	0.089	0.235	0.349	0.409	0.522	0.653	0.780	0.864	0.990	1.27
$\kappa \cdot 10^3\ \Omega^{-1}\ cm^{-1}$	10.63	12.19	16.0	18.58	19.30	20.66	22.72	26.45	28.52	28.5

• In Tables 1-5, where the ratio between the alkali metal halides and the corresponding halides of aluminum or antimony is larger than unity, deposits of undissolved salts were found at the bottom of the vessel.

TABLE 3

Change of the Specific Electrical Conductivity of the System $AlBr_3$–KBr–Nitromethane with a Change of the Ratio $\frac{KBr}{AlBr_3}$. $AlBr_3$: nitromethane = 1:20.5

Molecular ratio $\frac{KBr}{AlBr_3}$	0	0.214	0.392	0.615	0.750	1	1.2
$\kappa \cdot 10^3\ \Omega^{-1}\ cm^{-1}$	16.8	21.7	26.0	32.0	36.0	42.1	42.1

TABLE 4

Change of the Specific Electrical Conductivity of the System $AlCl_3$–NaCl–Nitromethane with a Change of the Ratio $\frac{NaCl}{AlCl_3}$*. $AlCl_3$: nitromethane = 1:7.43

Molecular ratio $\frac{NaCl}{AlCl_3}$	0	0.053	0.163	0.253	0.505	0.59	0.70	0.91	1.05
$\kappa \cdot 10^3\ \Omega^{-1}\ cm^{-1}$	6.8	8.2	20.7	24.5	29.5	37.4	40	48	50

The decomposition voltage of the ternary system was also studied. We used the usual system for determining the decomposition voltage. The value of a voltmeter graduation was 0.04 V and the sensitivity of the galvanometer was $1 \cdot 10^{-4}$ amp. Measurement was made at room temperature in a vessel with platinum point electrodes. The results of the measurements are presented in Table 6.

TABLE 5

Change of the Electrical Conductivity of the System $SbBr_3$–KBr–Nitromethane with a Change of the Ratio $\frac{KBr}{SbBr_3}$. $SbBr_3$: nitromethane = 1:1.96

Molecular ratio $\frac{KBr}{SbBr_3}$	0	0.311	0.45	0.55	0.67	0.83	1.05	1.19
$\kappa \cdot 10^3\ \Omega^{-1}\ cm^{-1}$	1.89	11.9	15.7	18.7	20.7	21.7	22	22

It should be pointed out that for the system KBr–$SbBr_3$ only one discontinuity was observed on the curve in the region of 0.6 V; it is possible that this decomposition voltage corresponds to the decomposition of HBr, which might be formed in small quantities as a result of hydrolysis. The high values of the decomposition voltage for systems containing an aluminum halide enabled us to assume that alkali metal deposited during electrolysis of the first three systems. The electrolysis experiments confirmed this.

TABLE 6

Decomposition Voltage of the Ternary Systems

Composition of the solution	Decomposition voltage (V)	Remarks
$\frac{AlBr_3}{\text{nitromethane}} = \frac{1}{9.5}$; $\frac{NaCl}{AlBr_3} = 1$	4.6	Solutions had deposits of insoluble alkali metal salts.
$\frac{AlCl_3}{\text{nitromethane}} = \frac{1}{7.43}$; $\frac{NaCl}{AlCl_3} = 1$	4.2	
$\frac{AlBr_3}{\text{nitromethane}} = \frac{1}{1.40}$; $\frac{KBr}{AlBr_3} = 1$	5.1	
$\frac{SbBr_3}{\text{nitromethane}} = \frac{1}{1.96}$; $\frac{KBr}{SbBr_3} = 1$	2.2	

The electrolysis was carried out in a U-shaped, curved tube with an internal diameter of 9 mm. A small plug of glass wool was placed in the bottom of the tube as a diaphragm. Platinum wires embedded in stoppers, sealed in glass tubes, served as the electrodes. The voltage of the battery was 12 V, and the current strength was 15 mA. During electrolysis of the systems $AlBr_3$–NaCl and $AlBr_3$–KBr, the liquid around the anode turned brown as a result of the bromide formed, and the cathode was covered with a dense deposit of antimony. A series of experiments on the electrolysis of the systems $AlBr_3$–NaCl and $AlCl_3$–NaCl was carried out, and the duration of the

* A. Ilchenko participated in the study of the electrical conductivities of the systems $AlCl_3$–NaCl and $AlBr_3$–KBr.

experiments varied from 1 to 3 hours. After completion of the electrolysis the cathode was removed and washed with dry gasoline, and after this it was immersed in a beaker of water. Phenolphthalein was added to the water and the alkali which formed was titrated. In some experiments, the current efficiency for sodium was 20-25%. During electrolysis of the systems of $AlBr_3$—KBr we also observed the deposition of metallic potassium, but we were unable to determine the current efficiency, since an explosion occurred during the removal of the electrode from the solution, and a large portion of the metallic potassium was discarded with the electrode. The electrode was washed with benzene and submerged in a beaker of water containing phenolphthalein. Thus, the deposition of potassium during the electrolysis was demonstrated qualitatively. The electrolysis of systems of $SbBr_3$—KBr was carried out in small beakers. Platinum wire served as the anode, as in previous experiments, and a plate of stainless steel with a surface of 1.5 cm^2 served as the cathode. The battery voltage was 4 V, and the current strength was 15 mA; the cathode was covered with a black deposit of antimony. The electrolysis was carried out for 1 hour. The current efficiency for antimony was 80%.

SUMMARY

1. An electrochemical investigation of nitromethane solutions was carried out for the systems $AlBr_3$—NaCl, $AlBr_3$—KBr, $AlCl_3$—NaCl, $SbBr_3$—KBr.

2. The solubility of the alkali metal halides in nitromethane solutions of the corresponding aluminum and antimony halides was investigated. The electrical conductivity, decomposition voltage and electrolysis were also studied.

3. On addition of alkali metal halides to solutions of the corresponding halides of aluminum and antimony in nitromethane, the specific electrical conductivity of the solutions increased.

4. The alkali metal halide ceased to dissolve when the ratio between the alkali metal halide and the corresponding halides of aluminum or antimony became equal to unity.

5. The investigation of the electrical conductivity and the solubility indicated the formation in the nitromethane solutions of complexes such as: $NaCl \cdot AlCl_3$, $NaCl \cdot AlBf_3$, $KbR \cdot AlBr_3$, $KBr \cdot SbBr_3$.

6. During electrolysis of solutions containing $AlBr_3$—NaCl, $AlCl_3$—NaCl, sodium deposited at the cathode; during the electrolysis of solutions of $AlBr_3$—KBr metallic potassium deposited at the cathode; and during electrolysis of solutions of $SbBr_3$—KBr antimony deposited at the cathode.

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SILICO-ORGANIC ESTERS OF PHOSPHORIC ACID — THE TRIS(TRIALKYLSILYL)PHOSPHATES

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The silico-organic esters of phosphoric acid — the tris(trialkylsilyl)phosphates $(R_3SiO)_3PO$ have hardly been described in the literature. There exists only a brief indication [1] that the formation of tris(trimethylsilyl)phosphate $[(CH_3)_3SiO]_3PO$ occurs on very slow distillation of hexamethyldisiloxane over a small amount of phosphoric anhydride. It should be pointed out that the silico-organic esters of the alkylphosphinic acids of the $R_3SiO(C_2H_5O)P(=O)C_2H_5$ type are described in the literature [2, 3], although opinions concerning their structures differ.

We found that the tris(trialkylsilyl)phosphates were formed smoothly in yields of 80% of the theoretical by heating hexalkyldisiloxanes with somewhat of an excess of phosphoric anhydride for a relatively short time. The reaction proceeds according to the scheme: $3R_3SiOSiR_3 + P_2O_5 \rightarrow 2(R_3SiO)_3PO$.

The rate of reaction decreased with an increase of the length of the radical in the original hexalkyldisiloxane. The tris(trialkylsilyl)phosphate was separated from the reaction mixture by vacuum distillation. By such a method we obtained two individual silico-organic esters of phosphoric acid, the properties of which are given in the Table.

TABLE

Tris(trialkylsilyl)phosphates

$(R_3SiO)_3PO$	Boiling point	Pressure (mm)	d_4^{20}	n_D^{20}	$n_F^{20}-n_C^{20}$	PO_4 content (in %) found	PO_4 content (in %) calculated
$[(CH_3)_3SiO]_3PO$	231.8°	749.5	0.9591	1.4089	0.0076	30.25, 30.16	30.20
	97.0						
$[(C_2H_5)_3SiO]_3PO$	200.5	11	0.9670	1.4457	0.0083	21.55, 21.58	21.55
	166.5	1					

These esters are colorless, viscous, practically odorless liquids. They are hydrolyzed by the action of aqueous alkali, which property we depended on as the basis for their quantitative determination. The rate of the hydrolysis reaction decreases with an increase of the length of the radical. The tris(trialkylsilyl)phosphates are rather stable thermally. Thus, for example, tris(trimethylsilyl)phosphate distills without decomposition at 232° at atmospheric pressure, but tris(triethylsilyl)phosphate distills at 370° almost undecomposed.

The higher hexalkyldisiloxanes — $(n\text{-}C_3H_7)_6Si_2O$ and $(n\text{-}C_4H_9)_6Si_2O$ — also react smoothly with P_2O_5.

Tris(tri-n-propylsilyl)phosphate and tris(tri-n-butylsilyl)phosphate are viscous liquids with boiling points of 215-225° and 260-270°, respectively, at 5 mm; they form in yields of about 55%. However, their separation in the analytically pure form is difficult because of their decomposition during distillation, even in a vacuum of 1 mm. It is interesting to note that, on vacuum distillation of the higher tris(trialkylsilyl)phosphates, the formation of phosphorescent decomposition products is observed.

EXPERIMENTAL*

The initial hexalkyldisiloxanes were obtained by reaction of hexachlorodisiloxane with suitable alkyl magnesium chlorides according to the scheme: $Cl_3SiOSiCl_3 + 6RMgCl \rightarrow R_3SiOSiR_3 + 6MgCl_2$ (R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$).

After purification by repeated distillation over metallic sodium (hexamethyl- and hexaethyldisiloxane — in the column), the initial hexalkyldisiloxane had the following constants:

* N. A. Dmitrieva participated in the experimental work.

R_6Si_2O	B.p. at a pressure of (mm)	d_4^{20}	n_D^{20}
$(CH_3)_6Si_2O$	100.4° (760)	0.7636	1.3774
$(C_2H_5)_6Si_2O$	236.3 (760)	0.8443	1.4340
$(n\text{-}C_3H_7)_6Si_2O$	285.5 (760)	0.8419	1.4418
$(n\text{-}C_4H_9)_6Si_2O$	171.5 (4)	0.8396	1.4460

Synthesis of tris(trimethylsilyl)phosphate. In a round-bottomed flask equipped with a ground-in reflux condenser connected to a wash bottle containing concentrated sulfuric acid and a thermometer, we placed 16.2 g (0.1 mole) of hexamethyldisiloxane and 7.1 g (0.05 mole) of phosphoric anhydride. The mixture was boiled for approximately 2 hours; thus, all of the phosphoric anhydride in solution was converted, and the temperature of the reaction mixture rose to 250°. The reaction product, a colorless liquid, was vacuum distilled. The yield of tris(trimethylsilyl)phosphate, with a b.p. of 94-98° (6 mm), was 16.0 g (77% based on the original hexamethyldisiloxane).

After redistillation, the substance had the constants given in the Table. The literature data [1] were: b.p. 85-87° (4 mm), n_D^{20} 1.4090.

Synthesis of tris(triethylsilyl)phosphate. 24.7 g (0.1 mole) of hexaethyldisiloxane and 5.2 g (0.037 mole) of phosphoric anhydride were heated gradually to 330°. Vacuum distillation of the reaction mixture gave 23.5 g (80%) of tris(triethylsilyl)phosphate with a b.p. of 200-205° (12 mm).

Analysis of the tris(trialkylsilyl)phosphates was carried out by titration with a 0.5 N solution of NaOH in a water or water-alcohol medium (indicator — methyl orange). The titration was made in the presence of a solution — "witness" — containing monosubstituted sodium phosphate. The analytical data are given in the Table.

SUMMARY

A method was proposed for the synthesis of the tris(trialkylsilyl)phosphates in high yields by reaction of the hexalkyldisiloxanes with phosphoric anhydride.

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OXONIUM COMPOUNDS OF ESTERS WITH ORGANIC ACIDS. I.

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At present, it is well-known that production of the final product of some reactions goes through the formation of intermediate oxonium complexes; therefore, the setting up of an investigation for the study of the oxonium properties of different substances was not lacking in theoretical as well as in practical interest. In this connection, we undertook a study of the oxonium properties of esters.

We studied: the ethyl esters of formic, acetic, monochloroacetic and trichloroacetic acids, the butyl, amyl, and cetyl esters of acetic acid, and the amyl ester of butyric acid. Choosing these objectives, we wanted to account for the effect of the length of the alkoxyl radicals and the nature of the functional groups, on the oxonium properties of the esters. We chose acetic, monochloroacetic and trichloroacetic acids, which differ considerably in their strengths, as the acid components. A total of 14 different systems with different properties was studied.

In the present report we present the results obtained from the following four systems: $CH_3COOC_2H_5$—CH_3COOH, $CH_3COOC_4H_9$—CH_3COOH, $CH_3COOC_5H_{11}$—CH_3COOH and $C_2H_7COOC_5H_{11}$—CH_3COOH. The densities and viscosities of all the systems were studied, and the vapor pressures of the first three were studied.

EXPERIMENTAL

The esters that we synthesized were subjected to repeated fractional distillation. The best fractions were distilled into ampoules in a special apparatus [1].

The acetic acid was purified by distillation and by fractional freezing and had a m.p. of + 16.67°.

The viscosity was measured by means of a viscosimeter, which is described in a report [2].

TABLE 1

$CH_3COOC_2H_5$—CH_3COOH

Percent ester		Viscosity (in centipoises)			Density (in g/ml)		
mole	weight	25°	40°	60°	25°	40°	60°
0.00	0.00	1.118	0.905	0.694	1.0442	1.0279	1.0074
10.20	14.19	0.970	0.791	0.618	1.0210	1.0045	0.9831
20.35	27.27	0.867	0.707	0.557	0.9994	0.9823	0.9603
30.37	39.03	0.771	0.634	0.503	0.9825	0.9642	0.9436
41.01	50.50	0.697	0.579	0.461	0.9644	0.9471	0.9247
49.79	59.28	0.644	0.538	0.430	0.9512	0.9354	0.9124
60.06	68.81	0.582	0.488	0.393	0.9379	0.9197	0.8933
69.62	77.08	0.543	0.454	0.369	0.9266	0.9086	0.8862
79.71	85.23	0.499	0.419	0.342	0.9141	0.8961	0.8731
90.48	93.31	0.460	0.388	0.316	0.9029	0.8849	0.8613
100.00	100.00	0.424	0.360	0.295	0.8914	0.8741	0.8505

Measurements of viscosity and density were made at the temperatures: 25, 40 and 60°. In all cases the measurements were made with freshly prepared mixtures.

Measurement of the vapor pressure was made by the dynamic method. For measuring the vapor pressure, we placed 65-70 ml of the liquid to be studied in an ebullioscope. The ebullioscope was provided with an external jacket, through which water was circulated from the ultrathermostat. The boiling points were measured at several pressures.

The partial vapor pressure was determined at 60°. The composition of the vapor was determined from the refractive index of the condensate.

Starting from the assumption of the additivity of the logarithms of the viscosities [3], we constructed semi-logarithmic curves of the viscosities of the systems studied.

In all cases, the viscosity was expressed in centipoises, the density in g/ml, and the vapor pressure in mm of Hg.

1. The System $CH_3COOC_2H_5 - CH_3COOH$

The results of the measurements of the viscosities and densities are given in Table 1, and are represented graphically in Fig. 1.

As is evident from Fig. 1, the isotherms of the logarithms of the viscosities were smooth curves, inclined convexly toward the composition axis.

TABLE 2

$CH_3COOC_2H_5 - CH_3COOH$

Mole % $CH_3COOC_2H_5$	Temperature / vapor pressure (in mm Hg)					
0.0	41.2°	44.5°	60.0°	64.1°	74.5°	83.5°
	37	45	93	110	171	249
21.4	42.0°	46.5°	51.2°	56.5°	60°	63.5°
	81	100	124	155	181	198
29.0	47.0°	50.0°	53.5°	56.5°	60°	62°
	137	159	178	203	229	251
49.2	52.5°	58.0°	60.0°	62.5°	67.5°	71.0°
	238	298	321	356	427	481
67.0	40.7°	45.0°	50.0°	54.0°	57.0°	60°
	165	199	241	282	319	360
89.0	46.0°	50.0°	52.6°	56.2°	60.0°	63.7°
	251	297	331	374	419	475
100.0	45.5°	48.5°	53.0°	58.0°	60.0°	63.5°
	250	282	337	411	444	499

The specific volume isotherms were almost straight lines (Fig. 1).

The results of the vapor pressure measurements are presented in Table 2.

The total vapor pressure isotherm (60°) (Fig. 1) of our system was concave toward the composition axis, i.e., the total vapor pressure values of the system were greater than for the ideal case.

The vapor pressure curves, and also the curves of the other properties of the system, reflect chiefly the association of acetic acid, and do not give a definite indication of the reaction with ethyl acetate, which, however, is not excluded by these data.

2. The System $CH_3COOC_4H_9 - CH_3COOH$

The results of the measurement of the viscosities and densities are presented in Table 3. In Fig. 2 are given the viscosity, vapor pressure, and specific volume curves.

It is obvious from Fig. 2 that the viscosity isotherms were complex at all temperatures. The viscosity isotherms were in almost all cases, convex toward the composition axis, and only in concentration ranges rich in ester (80-100%), proceeded as curves concave toward the composition axis. Such viscosity isotherms are related, in the present system, to the superposition of processes proceeding in opposite directions – the dissociation of the associated component and the chemical reaction.

The specific volume isotherms (Fig. 2) indicated expansion in the system. It is obvious from the specific volume curve that the decomposition of the associated acetic acid molecules is reflected to a greater degree on it than is the reaction.

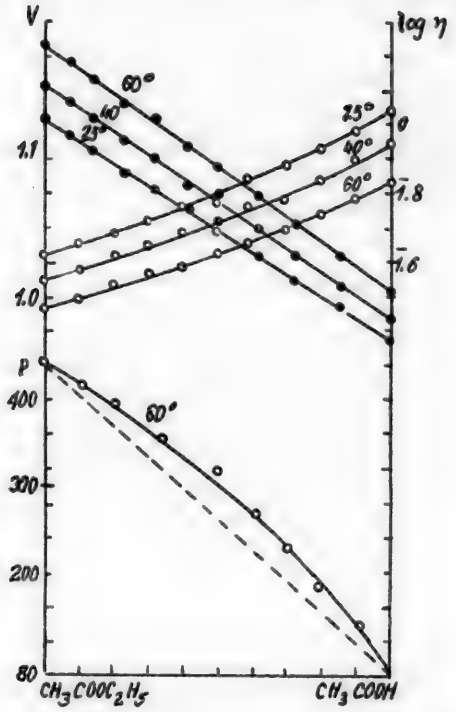

Fig. 1. Viscosity, vapor pressure (composition in mole percent) and specific volume (composition in weight percent) of the system $CH_3COOC_2H_5$—CH_3COOH.

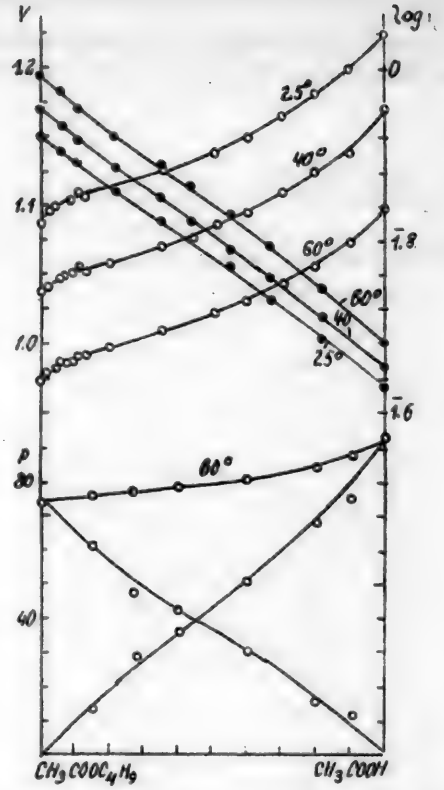

Fig. 2. Viscosity, vapor pressure (composition in mole percent) and specific volume (composition in weight percent) of the system $CH_3COOC_4H_9$—CH_3COOH.

TABLE 3

$CH_3COOC_4H_9$—CH_3COOH

Percent ester		Viscosity (in centipoises)			Density (in g/ml)		
mole	weight	25°	40°	60°	25°	40°	60°
0.00	0.00	1.118	0.905	0.694	1.0442	1.0279	1.0074
10.25	18.08	1.003	0.811	0.634	1.0062	0.9914	0.9711
20.35	33.06	0.947	0.767	0.595	0.9784	0.9611	0.9425
29.89	45.18	0.887	0.724	0.568	0.9559	0.9437	0.9202
39.98	56.29	0.842	0.685	0.543	0.9352	0.9232	0.9021
49.07	65.07	0.811	0.671	0.527	0.9247	0.9090	0.8898
64.49	77.83	0.770	0.630	0.499	0.9063	0.8923	0.8732
80.15	88.64	0.729	0.599	0.478	0.8905	0.8754	0.8581
87.05	92.86	0.716	0.589	0.467	0.8844	0.8709	0.8507
88.86	93.91	0.723	0.592	0.467	0.8830	0.8693	0.8497
90.96	95.11	0.712	0.583	0.460	0.8825	0.8669	0.8477
93.15	96.33	0.698	0.580	0.457	0.8808	0.8710	0.8473
94.27	96.95	0.698	0.580	0.457	0.8813	0.8684	0.8458
96.05	97.64	0.696	0.574	0.457	0.8776	0.8624	0.8435
97.79	98.85	0.686	0.563	0.450	0.8760	0.8627	0.8432
100.00	100.00	0.669	0.555	0.443	0.8739	0.8584	0.8396

Data on vapor pressure measurements are given in Table 4.

The relation of the total and partial vapor pressures to the composition (Fig. 2) is characterized by the negative slope from Raoult's Law.

The total and partial vapor pressure curves passed through a discontinuity point. Such vapor pressure isotherms are observed in systems involving chemical interaction.

Thus, the experimental data enable us to assert that the chemical interaction takes place in the system butyl acetate–acetic acid. The system does not conduct the electric current.

TABLE 4

$CH_3COOC_4H_9$–CH_3COOH

Mole % $CH_3COOC_4H_9$	Temperature / vapor pressure (in mm Hg)					
0.0	41.2°	44.5°	60.0°	64.1°	74.5°	83.5°
	37	45	93	110	171	249
9.9	40.0°	61.5°	58.5°	60.0°	66.5°	72.5°
	33	101	89	88	118	158
19.9	56.0°	60.0°	69.0°	75.0°	48.5°	53.2°
	68	84	131	162	48	61
40.0	55.2°	60.0°	63.0°	67.0°	72.5°	–
	64	81	93	110	134	–
60.0	39.0°	47.2°	54.5°	60.0°	65.5°	–
	28	43	61	79	95	–
72.9	37.5°	47.5°	54.0°	60.0°	65.5°	70.5°
	28	44	600	77	94	116
85.0	43.0°	48.5°	54.00°	60.0°	65.0°	–
	39	51	67	76	95	–
100.0	43.0°	48.5°	55.00°	60.0°	65.0°	70°
	38	45	60	74	93	114

TABLE 5

$C_3H_7COOC_5H_{11}$–CH_3COOH

Percent ester		Viscosity (in centipoises)			Density (in g/ml)		
mole	weight	25°	40°	60°	25°	40°	60°
0.00	0.00	1.12	0.905	0.694	1.0442	1.0279	1.0074
10.13	22.90	1.06	0.853	0.662	0.9917	0.9745	0.9547
14.99	31.74	1.04	0.836	0.653	0.9719	0.9562	0.9376
20.07	39.83	1.02	0.824	0.644	0.9558	0.9424	0.9232
25.15	46.97	1.03	0.827	0.642	0.9435	0.9286	0.9097
30.14	58.21	1.03	0.833	0.645	0.9323	0.9182	0.8990
40.00	63.73	1.04	0.833	0.645	0.9142	0.9006	0.8808
49.99	72.49	1.05	0.846	0.656	0.8992	0.8881	0.8688
60.18	79.93	1.07	0.850	0.657	0.8886	0.8756	0.8559
69.19	85.55	1.08	0.859	0.665	0.8809	0.9679	0.8499
80.40	91.53	1.08	0.860	0.661	0.8721	0.8594	0.8418
89.06	95.54	1.08	0.861	0.667	0.8666	0.8530	0.8364
94.59	97.88	1.07	0.859	0.664	0.8632	0.8507	0.8330
100.00	100.00	1.07	0.860	0.664	0.8599	0.8480	0.8317

The results of the viscosity and density measurements are presented in Table 5. The viscosity and specific volume curves are represented in Fig. 3. The isotherms of the logarithm of the viscosity passed through a minimum, at approximately 20-30 mole % amyl butyrate, and through an indistinct maximum. As we have already pointed out, such isotherms of the logarithm of the viscosity indicate the presence of chemical interaction in the system. The appearance of the minimum, obviously, was connected with the decomposition of the associated acetic acid molecules under the influence of the addition of a second component; this leads to a sharp decrease of the viscosity, masking the increase due to the interaction of the components of the system.

The specific volume curve (Fig. 3) indicated expansion in the system. Obviously, the decomposition of the associated acid molecules is reflected to a greater extent on it, than is the chemical interaction.

On the basis of what has been presented, it can be stated that chemical interaction does occur in the system $C_3H_7COOC_5H_{11}$–CH_3COOH. The absence of electrical conductivity indicates that this chemical interaction is not an acid-base interaction.

4. The System $CH_3COOC_5H_{11}$ – CH_3COOH

The results of the measurements of viscosity and density of the system at 25, 40 and 60° are presented in Table 6. In Fig. 4 are the viscosity, vapor pressure and specific volume curves.

It is evident from the curves of the logarithms of viscosity versus the composition, constructed from the data of Table 6 (Fig. 4), that the isotherms of the logarithms of viscosity pass through a minimum and a maximum. A shift of the maximum and minimum toward the ester side occurs at elevated temperatures.

It may be assumed, from the course of the isotherms of the logarithm of viscosity, that the complexes forming in the system are unstable and are subject to decomposition at elevated temperatures. The specific volume isotherms are straight lines. Obviously, the linear nature of the specific volume isotherms is connected with the mutual compensation of the chemical interaction and the decomposition of the associated molecules.

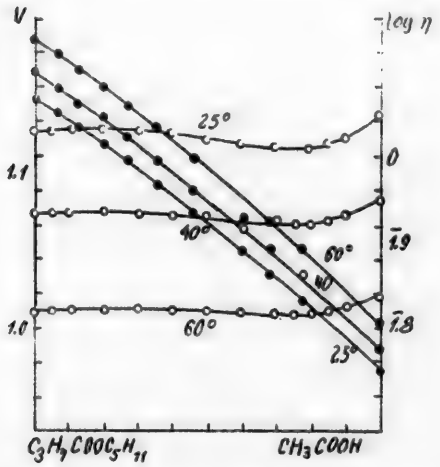

Fig. 3. Viscosity (composition in mole percent) and specific volume (composition in weight percent) of the system $C_3H_7COOC_5H_{11}$–CH_3COOH.

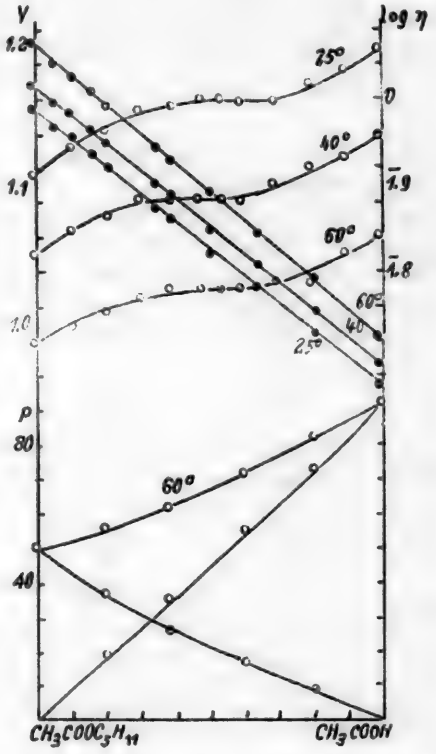

Fig. 4. Viscosity, vapor pressure (composition in mole percent), and specific volume (composition in weight percent) of the system $CH_3COOC_5H_{11}$–CH_3COOH.

The results of the measurements of the relation of boiling point to pressure are presented in Table 7.

The isotherms of both the total and partial vapor pressure (Fig. 4) deviated negatively from the ideal case. Thus, it can be stated that the components of the system, amyl acetate–acetic acid react chemically. The system proved to be electrically non-conducting. As in the preceding cases, it is obvious that the interaction is not of an acid-base nature.

SUMMARY

1. The densities and viscosities of the systems $CH_3COOC_2H_5$–CH_3COOH, $CH_3COOC_4H_9$–CH_3COOH, $CH_3COOC_5H_{11}$–CH_3COOH and $C_3H_7COOC_5H_{11}$–CH_3COOH were studied at 25, 40 and 60°.

2. The vapor pressures of the systems $CH_3COOC_4H_9$–CH_3COOH, $CH_3COOC_5H_{11}$–CH_3COOH and $CH_3COOC_2H_5$–CH_3COOH were studied.

TABLE 6

$CH_3COOC_5H_{11}$–CH_3COOH

Percent ester		Viscosity (in centipoises)			Density (in g/ml)		
mole	weight	25°	40°	60°	25°	40°	60°
0.00	0.00	1.118	0.905	0.694	1.0442	1.0279	1.0074
9.45	18.45	1.055	0.853	0.669	1.0043	0.9868	0.9649
20.18	35.41	1.049	0.831	0.613	0.9740	0.9560	0.9340
30.35	48.58	0.994	0.799	0.616	0.9497	0.9332	0.9090
40.48	59.59	0.978	0.781	0.603	0.9278	0.9122	0.8905
45.99	64.86	1.002	0.797	0.609	0.9180	0.9040	0.8820
51.17	69.44	1.006	0.798	0.609	0.9090	0.8965	0.8760
60.74	77.04	0.980	0.777	0.595	0.8940	0.8800	0.8610
69.57	83.22	0.974	0.772	0.589	0.8840	0.8700	0.8525
78.78	88.95	0.917	0.734	0.566	0.8740	0.8620	0.8440
89.12	94.67	0.881	0.708	0.547	0.8680	0.8550	0.8370
100.00	100.00	0.818	0.663	0.522	0.8629	0.8491	0.8272

TABLE 7

$CH_3COOC_5H_{11}$–CH_3COOH

Mole % $CH_3COOC_5H_{11}$	Temperature vapor pressure (in mm Hg)					
0.0	41.2°	44.5°	60.0°	64.1°	74.5°	83.5°
	37	45	93	110	171	249
19.9	39.5°	46.0°	50.7°	55.7°	60.0°	64.5°
	31	45	55	69	82	98
40.0	41.5°	45.5°	50.7°	56.0°	60.0°	66.0°
	29	37	43	56	71	94
61.7	43.0°	49.5°	55.0°	60.0°	64.5°	–
	28	39	56	62	81	–
80.8	42.0°	47.5°	56.5°	60.0°	63.7°	–
	22	35	53	56	59	–
100.0	45.0°	51°	56.0°	60.0°	63.0°	–
	28	36	45	49	56	–

3. In the systems studied, it was observed that the interaction was intensified in proportion to the increase in length of the alkyl radical of the alcoholic part of the ester.

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OXONIUM COMPOUNDS OF ESTERS WITH ORGANIC ACIDS

II. THE SYSTEM CETYL ACETATE—ACETIC ACID

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Physico-chemical analysis of systems [1] formed by esters and acetic acid showed that acetic acid reacts with the esters, with the formation of associative type complexes; thus, it was proved that the longer the alcoholic radical of the ester, the greater the extent to which the interaction occurred. Continuing the systematic study of the oxonium properties of esters, we felt it of interest to study the behavior of acetic acid in relation to an ester with a possibly longer alcohol radical. We selected cetyl acetate as the ester and studied the viscosity and density of the system $CH_3COOC_{16}H_{33}$—CH_3COOH at temperatures of 40, 50, 60 and 70°.

TABLE

Percent ester		Viscosity η (in centipoises)				Density (in g/ml)			
mole	weight	40°	50°	60°	70°	40°	50°	60°	70°
0.00	0.00	0.905	0.767	0.694	0.607	1.0279	1.0162	1.0074	0.9958
9.34	32.91	1.46	1.25	1.09	0.956	0.9583	0.9487	0.9385	0.9280
28.74	65.79	2.58	2.13	1.83	1.59	0.9019	0.8911	0.8839	0.8755
51.08	83.33	3.72	2.99	2.47	2.12	0.8734	0.8649	0.8570	0.8499
68.55	92.34	4.39	3.50	2.86	2.37	—	—	—	—
100.00	100.00	5.01	3.85	3.20	2.67	0.8455	0.8379	0.8310	0.8238

The cetyl acetate was synthesized by a method described earlier [1]. For purification, the cetyl acetate was vacuum distilled twice. The fraction boiling at a temperature of 174-176° and at a pressure of 12 mm, was collected and subjected to fractional freezing. The cetyl acetate had a m.p. of 24°. The acetic acid was purified by distillation and by fractional freezing and had a m.p. of 16.67°.

Results of the viscosity and density measurements are given in the Table.

It is obvious from Fig. 1 that the viscosity isotherm, at 40°, suggests an S-shaped curve. At elevated temperatures, the viscosity isotherms become concave toward the abscissa along their entire lengths. Such a change of the viscosity isotherm is apparently connected with the decomposition of associated acetic acid molecules at elevated temperatures. This leads to the fact that the interaction between the components is reflected more distinctly on the viscosity isotherms at high temperatures (especially at 70°).

The specific volume curve (Fig. 2) was a straight line. It can be assumed that the mutual compensation of the processes (chemical interaction and decomposition of the associated acetic acid molecules) occurring in the system is reflected to a greater extent on the specific volume isotherms than on the viscosity isotherms.

SUMMARY

1. The viscosities and densities of the system, $CH_3COOC_{16}H_{33}$—CH_3COOH, were studied at 40, 50, 60 and 70°.

2. It was found that interaction occurs in the system. A comparison of the results obtained in the study of the behavior of acetic acid toward ethyl acetate, butyl acetate, amyl butyrate and amyl acetate, with the behavior of acetic acid toward cetyl acetate, showed that interaction occurs to the greater degree in the system, $CH_3COOC_{16}H_{33}$—CH_3COOH.

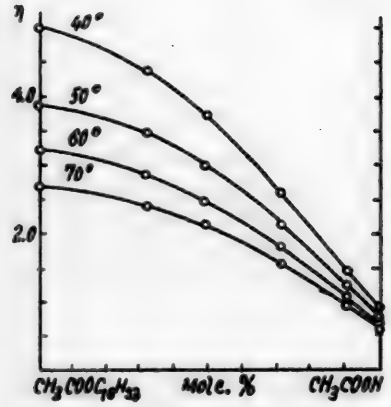

Fig. 1. Viscosity of the system, cetyl acetate—acetic acid.

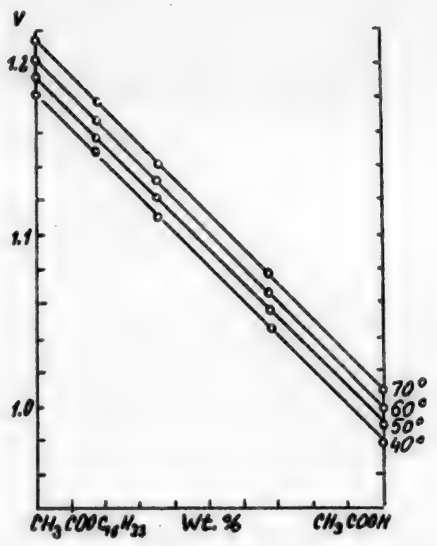

Fig. 2. Density of the system, cetyl acetate—acetic acid.

3. We confirmed the observations made earlier, that the longer the alcohol radical of the ester, the greater the degree to which interaction occurs between the acid and the ester.

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ISOMERIZATION OF METHYLCYCLOHEXANE AND ETHYLCYCLOHEXANE IN THE PRESENCE OF ALUMINUM CHLORIDE UNDER PRESSURE OF HYDROGEN

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We showed [1] that cyclohexane, at a high temperature and under pressure of hydrogen, in the presence of aluminum chloride, isomerizes to methylcyclopentane, the content of which in the catalyzate fraction corresponding to the composition C_6H_{12}, amounts to 50.6% in experiments carried out at 150°, and 63.5% in experiments made at 200°. Hydrogen in thiscase inhibited cracking.

In this investigation, we were interested in the relation of the behavior of methylcyclohexane and ethylcyclohexane. As is known, at temperatures up to approximately 100°, the equilibrium between the cyclohexane and the cyclopentane hydrocarbons of the compositions C_7H_{14} and C_8H_{16} is shifted practically completely toward the side of the cyclohexane hydrocarbons [2]. The only transformation which ethylcyclohexane and the higher homologs of cyclohexane underwent was disproportionation of the side chain, as a result of which polymethylcyclohexanes formed. However, at elevated temperatures the content of the cyclopentane hydrocarbons in the equilibrium mixture increased. For example, Puchkov and Nikolaeva [3] showed that, in the presence of molybdenum disulfide at 400° and at a hydrogen pressure of approximately 350-370 atm, methylcyclohexane was isomerized, and formed a mixture of cyclopentane hydrocarbons: 1,2- and 1,3-dimethylcyclopentanes and some ethylcyclopentane. However, under the conditions studied, cracking, with formation of branched paraffin hydrocarbons, was very significant.

In the present work, we showed that, at temperatures of 150-250°, in the presence of aluminum chloride, and under a hydrogen pressure of about 100 atm, methylcyclohexane formed a mixture of 1,1-, 1,2- and 1,3-dimethylcyclopentanes, in which the 1,3-dimethylcyclopentane predominated. At 250°, ethylcyclohexane formed a mixture of 1,1-, 1,2-, 1,3- and 1,4-dimethylcyclohexanes and substituted cyclopentane hydrocarbons, among which we observed 1,1,2-, 1,1,3-, 1,2,3- and 1,2,4-trimethylcyclopentanes. The presence of 1,1-dimethylcyclopentane, 1,1-dimethylcyclohexane, and also 1,1,2- and 1,1,3-trimethylcyclopentanes among the isomerization products enabled us to assume that, under the conditions studied, the isomerization was definitely similar to the transformation of the homologs of cycloheptane during catalytic dehydrogenation on platinum, which proceeds evidently [4], through the stage of formation of the semi-disubstituted homolog of cyclohexane.

EXPERIMENTAL

The initial hydrocarbons, obtained by hydrogenation of toluene and ethylbenzene with a selective nickel catalyst under pressure, had the following properties:

Methylcyclohexane: b.p. 101.5° (760 mm), n_D^{20} 1.4230, d_4^{20} 0.7692. Literature data [5]: b.p. 100.93° (760 mm), n_D^{20} 1.42312, d_4^{20} 0.76939.

Ethylcyclohexane: b.p. 130.2° (760 mm), n_D^{20} 1.4356. Literature data [5]: b.p. 131.78° (760 mm), n_D^{20} 1. 43304, d_4^{20} 0.78792.

The initial ethylcyclohexane contained traces of ethylbenzene, from which it was not freed, since in isomerization with aluminum chloride a small quantity of aromatic hydrocarbons was not only unharmful, but also inhibited the cracking reaction.

The isomerization was carried out in a 150 ml revolving autoclave (40 r.p.m.) of stainless steel. 50 g of the hydrocarbon and 5 g of technical aluminum chloride were charged into the autoclave, after which hydrogen was supplied, and the autoclave was heated rapidly to the reaction temperature. After suitable exposure at the required temperature, it was quickly cooled to 0°.

Experiments with methylcyclohexane. The isomerization of methylcyclohexane was carried out at 150, 200 and 250°, and at an initial hydrogen pressure from 70 to 120 atm. After washing the catalyzate with solutions of soda and water, and drying, we distilled it, using a column with an efficiency of 30 theoretical plates. As an example, in Table 1 we present the results of the distillation of the catalyzate obtained at 200°.

TABLE 1

Results of the Fractional Distillation of the Catalyzate of Methylcyclohexane

Fraction	Boiling point	Yield (in vol. %)	n_D^{20}	d_4^{20}	Critical temperature of solution in aniline
1	To 88.5°	7.8	–	–	–
2	88.5-89.5	19.7	1.4089	0.7398	50.9°
3	89.5-90.7		1.4091	0.7427	49.8
4	90.7-99.0	10.0	–	–	–
5	99.0-100.5	52.3	1.4222	–	40.4
	Residue	10.2	–	–	–

From a consideration of the indices of refraction, specific gravities, and especially, the aniline points, it followed that the 2nd and 3rd fractions were mixtures of cyclopentane hydrocarbons, and did not contain paraffin hydrocarbons, but the 5th fraction corresponded to the initial methylcyclohexane. From distillation data, it is possible to estimate roughly the content of the cyclopentane homologs in the catalyzate.

In Table 2 we present the results of experiments on the isomerization of methylcyclohexane at different temperatures.

TABLE 2

Isomerization of Methylcyclohexane

Expt. No.	Temperature	Initial pressure (atm)	Length of time of experiment (hours)	Yield of liquid product (%)	Composition of isomerization products (%)			
					head fraction	C_7H_{14} fraction	residue	dimethylcyclopentane content in C_7H_{14} fraction
19	150°	120	3.5	87.2	12.6	77.8	9.6	23.5
18	200	70	0.5	87.0	7.8	82.0	10.2	30.1
17	250	110	0.5	78.6	14.4	61.4	24.2	45.1

Thus, the content of cyclopentane hydrocarbons in the catalyzate obtained at 250° was 28%, whereas that of the catalyzate obtained at 200° was 25%, and at 150° – only 18%. It should be noted that the isomerization of methylcyclohexane was accompanied to a greater degree by side reactions than was the isomerization of cyclohexane [2].

Because of their small quantities, the fractions obtained from experiments carried out under different conditions, but having identical boiling points, were combined and analyzed optically by means of their Raman spectra. The apparatus, materials, methods of exposure, of interpolation and of calculation were described earlier [6]. Below are presented the spectra for the fractions with b.p. of 88.5-89.5° and with a b.p. of 89.5-90.7°. In parentheses after the frequencies are given the degrees of blackening, as determined from the photomicrographs (distance from the peak of the line to the background of the plate).*

Spectrum of the 88.5-89.5° fraction. $\Delta\nu$ cm^{-1}: 257(4); 306 (3); 350 (4); 426 (4); 497 (11); 527 (8); 547 (0); 561 (11); 590 (4); 726 (6); 769 (13); 805 (15); 828 (17); 862 (3); 886 (0); 895 (14); 956 (9)dl; 984 (14); 1026–1041 (8)dl; 1082 (14); 1099 (22); 1144 (20); 1341–1360 (10)dl; 1447–1460 (34) w, dl.

Spectrum of the 89.5-90.7° fraction.. $\Delta\nu$ cm^{-1}: 257 (4); w, dl; 350 (2); 426 (3); 497 (15); 514-527 (10)dl; 550-561 (5)dl; 605 (5); 769 (15)w, dl; 805 (17); 828 (16); 862 (5); 895 (14); 956 (7)dl; 984 (12); 1030 (5)w, dl; 1080 (14); 1099 (19); 1140-1152 (19)dl; 1230 (2); 1293 (11); 1311 (10); 1341-1360 (12)dl; 1460 (34)w, dl.

A comparison of the spectra of the fractions with literature data on the spectra of the dimethylcyclopentanes [7, 8], and a comparison of the constants of these fractions (Table 1) with the constants of the cyclopentane hydrocarbons with the general formula C_7H_{14} (Table 3), enabled us to assume that both fractions contained the stereoisomers 1,3-dimethylcyclopentane, trans-1,2-dimethylcyclopentane and 1,1-dimethylcyclopentane. The presence of

* For the spectra, the following abbreviations are used: w – wide line (band); d – diffuse; s – sharp; dl – double line (close doublet); b line in the background of considerable intensity.

paraffin hydrocarbons, which could be formed in appreciable quantities as a result of the rupture of the ring, was excluded, since they were absent from the strongest analytical lines [8, 9, 10], and since the aniline points of the fractions corresponded to the aniline points of the cyclic hydrocarbons.

TABLE 3

Properties of the Dimethylcyclopentanes [5]

Hydrocarbon	Boiling point	n_D^{20}	d_4^{20}	Critical temperature of solution in aniline
1,1-Dimethylcyclopentane	87.84°	1.41357	0.75448	45.0°
trans-1,2-Dimethylcyclopentane	91.87	1.41199	0.75144	46.7
cis-1,2-Dimethylcyclopentane	99.53	1.4221	0.77262	47.8
trans-1,3-Dimethylcyclopentane	90.77	1.40891	0.74479	49.9
cis-1,3-Dimethylcyclopentane	91.9	1.4111	0.7488	–

On the basis of the intensities of the analytical lines of the pure hydrocarbons [1,3-dimethylcyclopentane: 514 (13) and 828 (28); 1,1-dimethylcyclopentane: 562 (20); and trans-1,2-dimethylcyclopentane: 497 (35) and 896 (34)] and the degree of blackening of the corresponding lines in spectra of the fractions, and by a consideration of the relative quantities of the fractions, an approximate calculation of the quantitative composition was made. It was found that in the mixture of the cyclopentane homologs there was approximately 55% 1,3-dimethylcyclopentane approximately 25% trans-1,2-dimethylcyclopentane, and about 20% 1,1-dimethylcyclopentane.

Moreover, in fraction 5, according to its boiling point, there could be both cis-1,2-dimethylcyclopentane (Table 1), and unaltered methylcyclohexane; however, the aniline point of this fraction (40.4°) agreed with that for pure methylcyclohexane (40.3°), and differed greatly from that for cis-1,2-dimethylcyclopentane (47.8°). As to the analysis of the spectral data for the 2nd and 3rd fractions, although the spectrum of cis-1,2-dimethylcyclopentane was close to the spectrum of the corresponding trans-isomer, the strongest line in the spectrum of cis-1,2-dimethylcyclopentane, $\Delta\nu$ 888 (38), was observed at the edge in the spectrum of the 88.5-89.5° fraction, but it was absent from the spectrum of the 89.5-98.7° fraction. Hence, we concluded that if cis-1,2-dimethylcyclopentane also was present in the catalyzate, then it was in a negligible quantity.

We turn our attention now to the presence of 1,1-dimethylcyclopentane in the catalyzate, in spite of the fact that at the lower temperatures it readily and completely isomerizes to methylcyclohexane [11].

The isomerization of ethylcyclohexane was carried out only at a temperature of 250°, and at an initial hydrogen pressure of 110 atm. As a result of three parallel experiments, 150 g of hydrocarbon was treated in the presence of 15 g of aluminum chloride. The duration of the experiment was 30 minutes. After washing and drying, 125 g of hydrocarbons was obtained.

Since during the isomerization of ethylcyclohexane a complex mixture of isomers might form, which is impossible to analyze by means of only one distillation, the isomerizate was subjected to a preliminary catalytic dehydrogenation at 300°, according to Zelinsky, in the presence of a platinum-iron catalyst [12], and at a volume rate of 0.9. A total of 80 g was dehydrogenated. After dehydrogenation, the index of refraction of the catalyzate was n_D^{20} 1.4599. Repeated passage of a small portion of the primary catalyzate over the catalyst led to only negligible increases of the index of refraction. The aromatic hydrocarbons which formed as a result of the dehydrogenation of the cyclohexane homologs were separated by Tsvet's chromatographic method, with the use of silica gel as the adsorbent. From 68 ml we obtained 36 ml of aromatic hydrocarbons and 18.5 ml of cyclopentane hydrocarbons and 1,1-dimethylcyclohexane. The remaining cyclanes were distilled, and the fractions obtained had the properties listed in Table 4.

The Raman spectra of the fractions with b.p. of 107-116° and b.p. of 116-120.2° were studied. These spectra are presented below.

Spectrum of the 107-116° fraction. $\Delta\nu$ cm^{-1}: 257 (4)d, b; 340 (3,5)d, b; 411 (6) d, w; 493 (17); 528 (14) dl; 570 (4)d; 603 (4)d; 706 (5)d; 746 (4); 769 (22)s; 792 (6)b; 811 (13)b; 875 (6); 886 (3); 938 (11); 966 (3); 992 (5); 1026 (3)b; 1057 (3)b; 1101 (16)b, 1157 (18)w; 1188 (16.5); 1226 (5); 1287 (9); 1307 (10); 1346 (13); 1380 (9); 1408 (4); 1460 (40)w.

Spectrum of the 116-120.2° fraction. $\Delta\nu$ cm^{-1}: 322 (3)b; 357 (2); 406 (5)d; 430 (5)d; 460 (4); 492 (5, 5); 523 (7); 557 (8); 603 (3)d; 646 (4); 681 (0); 704 (26)s; 746 (10); 769 (12); 808 (4); 827 (11, 5); 850 (4); 871 (3); 890 (2, 5); 912 (4, 5); 938 (6, 5); 960 (6); 988 (6); 1026 (11)d; 1079 (12)w; 1095 (13)w; 1133-1144 (14)dl, b; 1192 (17); 1246 (5); 1266 (5); 1296 (12)w; 1353 (12)w; 1382 (4); 1451 (38).

TABLE 4

Boiling point	Quantity (ml)	n_D^{20}	d_4^{20}	Aniline point
To 107°	5	—	—	—
107-116	8.5	1.4118	0.7499	56.8°
116-120.2	3.0	1.4194	0.7637	50.1
Residue	1.0	—	—	—

TABLE 5

Fraction	Boiling point	Quantity (ml)	n_D^{20}
1	50-100°	0.2	1.4664
2	100-128	1.8	1.4611
3	128-140	26.1	1.4959
4	140-150	4.8	1.5020
Residue	—	1.6	—

A comparison of these data with the spectra of the octane, dimethylcyclohexane and trimethylcyclopentane hydrocarbons [7-11, 13] showed that the chief components of the 107-116° fraction were the $1^c,2^t,4^c$-, 1,1,3-, and $1^c,2^t,3^c$-trimethylcyclopentanes. The 116-120.2° fraction also consisted mainly of trimethylcyclopentanes (more likely $1^c,2^t,4^c$-, $1^c,2^t,3^c$-, $1^c,2^c,3^t$-, $1^c,2^c,3^c$- and 1,1,2-trimethylcyclopentanes), but apart from this, 1,1-dimethylcyclohexane was present in considerable quantity in the fractions. The 1,1-dimethylcyclohexane content in these fractions was determined by the internal standard method. In the spectrum of the fraction, the ratio of the intensity of the 704 cm^{-1} line to the intensity of the 669 cm^{-1} of chloroform was measured photometrically, added to a definite quantity, and on the basis of data [8] on the intensity of the 706 cm^{-1} line in the spectrum of pure 1,1-dimethylcyclohexane, its content in the fraction was calculated as about 30%.

The aromatic hydrocarbons which were formed by the dehydrogenation of the cyclohexane homologs (with admixture of a certain quantity of roughly separated cyclopentane hydrocarbons) were distilled into fractions represented in Table 5.

In the 1st and 2nd fractions, the presence of a small quantity of toluene and benzene is possible. The 3rd and 4th fractions represent a xylol fraction. They were combined (n_D^{20} 1.4968, d_4^{20} 0.8652), after which on one portion the Raman spectrum was determined, and the other was oxidized by an alkaline solution of permanganate. From the oxidation, a very small quantity of benzoic and o-phthalic acids, a certain quantity of terephthalic acid, and a large quantity of isophthalic acid, were obtained. The two latter acids were identified by conversion to the corresponding dimethyl esters.

The spectrum of the aromatic fraction with a b.p. of 128-150° is presented below.

Spectrum of the 128-150° fraction. $\Delta\nu$ cm^{-1}: 177 (2)b; 202 (2)b; 233 (2)w, b; 257 (1); 277 (2)b; 313 (3,5)w; 386 (0); 402 (2)d, w; 460 (6); 482 (2); 507 (1); 518 (7); 535 (10); 583 (5); 621 (3); 644 (5); 671 (3); 702 (2)dl; 726 (16); 737 (10); 770 (5); 811 (7); 827 (14); 846 (10); 893 (3)d; 945 (6); 968 (3)w; 1001 (22); 1033 (9); 1054 (10); 1094 (4)d; 1152 (7)w; 1170 (5)b; 1183 (5)b; 1205 (15); 1224 (7); 1251 (12); 1267 (5, 5); 1290 (3)w; 1317 (2); 1346 (1, 5); 1380 (16, 5); 1451 (8)w, d; 1583-1590 (6)dl; 1605-1617 (20)dl.

From the data on the most characteristic lines [14], we identified o-, m- and p-xylenes and ethylbenzene. A quantitative determination of these hydrocarbons was carried out by a rigorous photometric method, with the use of the following analytical lines: p-xylene 459 (200) and 829 (410), m-xylene 538 (229), o-xylene 582 (213), and ethylbenzene 622 (47).

The composition of the 128-150° fraction showed the following: o-xylene 16%, m-xylene 45%, p-xylene 20%, ethylbenzene 19%.

Thus, the initial ethylcyclohexane, on reaction with aluminum chloride at 250°, was converted to a mixture of hydrocarbons with approximately the following composition: 12% unaltered ethylcyclohexane, 3% 1,1-dimethylcyclohexane, 10% 1,2-dimethylcyclohexane, 13% 1,4-dimethylcyclohexane, 30% 1,3-dimethylcyclohexane, 20% cyclopentane hydrocarbons (among them 1,1,2-, 1,1,3-, 1,2,3- and 1,2,4-trimethylcyclopentanes), and 12% hydrocarbons of higher and lower molecular weights than the initial ethylcyclohexane.

SUMMARY

The isomerization of methylcyclohexane and ethylcyclohexane, in the presence of aluminum chloride and hydrogen at elevated temperatures, and at an initial hydrogen pressure of about 100 atm, was studied. The catalyzates of methylcyclohexane included a mixture of cyclopentane hydrocarbons approximately in the quantity: at 150° — 18%, at 220° — 25% and at 250° — 28%. The 1,3-isomer predominated in the mixture of 1,1-, 1,2- and 1,3-dimethylcyclopentanes obtained.

The catalyzate obtained at 250° from ethylcyclohexane contained about 20% cyclopentane hydrocarbons (1,1,2-,1,1,3-, 1,2,3- and 1,2,4-trimethylcyclopentanes) and approximately 12% unaltered ethylcyclohexane, 30% 1,3-dimethylcyclohexane, 13% 1,4-dimethylcyclohexane, 10% 1,2-dimethylcyclohexane and 3% 1,1-dimethylcyclohexane.

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* See Consultants Bureau Translation, page 2409.

** See Consultants Bureau Translation, page 607.

CATALYTIC AMINATION OF ORGANIC COMPOUNDS

II. CATALYTIC AMINATION OF PHENOLS

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The catalytic amination of phenols by ammonia is of great interest from both the theoretical and practical points of view. The replacement of the inactive phenolic hydroxyl group by the amino group has been very inadequately studied, but the primary aromatic amines produced by this reaction, as is known, are of very great practical value.

All attempts to replace the hydroxyl group of the phenols by the amino group, by the action of ammonia on phenols at ordinary pressures, in the presence of different catalysts, have been almost entirely unsuccessful [1], or have given amine yields of 10-12%, on the basis of the amount of phenol reacting [2]. Only by carrying out these reactions with compressed ammonia, were we able to increase the amine yield to 80%. Among the different oxides which were used as catalysts in these reactions, the most active proved to be aluminum oxide [3]. This reaction has been used for the amination of the phenols from coal-tar fractions [4], and in recent years has been reflected in a number of patent claims [5].

This reaction was further studied in the present work. As the catalyst, we used commercially-produced, active aluminum oxide, i.e., a catalyst of the standard type. The amination reaction was studied at different temperatures and ammonia pressures. The following phenols underwent amination: phenol, o- and p-cresol, m-xylenol, o-hydroxydiphenyl and thymol. The two latter compounds had not been subjected to amination until now.

The method of our investigations included the following: the experiments were carried out in a somewhat improved apparatus, as compared with that which was described earlier in the work of one of us [3]. Phenol vapors were passed at a controlled rate over a heated catalyst in a current of compressed ammonia. The catalyst was

TABLE 1

Relation of Aniline Yield to the Ammonia Pressure. Temperature 475°; rate of passage of phenol — 6 drops per minute

Quantity of phenol (g)	Pressure of ammonia (atm)	Yield (g)		Aniline yield (%) based on phenol	
		aniline	phenol	taken	reacting
13	9.5	10.2	1.2	79.3	88.3
13	7.0	9.0	1.0	70.0	75.8
18	6.0	4.0	12.3	22.5	71.00
18	1.0	3.0	14.0	16.8	76.00

processed by the usual methods, the amines were separated with a solution of hydrochloric acid, and the unreacted phenols were separated by a solution of alkali. The amines were studied; no secondary or tertiary amines were found among them; the primary amines were characterized by their acetyl derivatives, and also by their physical constants. The relation of the aniline yield to the temperature and to the ammonia pressure in the reaction zone was established. The data that we obtained are presented in Tables 1 and 2.

The data of Tables 1 and 2 show that, the higher the ammonia pressure in the reaction zone, the larger the aniline yield. The largest aniline yield was observed at 475°. It should be noted that the catalyst retains its activity for about 20 hours, after which it may be regenerated. At 500° the catalyst rapidly loses its activity because of coking.

In the amination of 13 g of o-cresol at 475°, at an ammonia pressure of 9 atm, and at a rate of passage of o-cresol of 6 drops per minute, we obtained 7.5 g of o-toluidine with a b.p. of 198-202° (d_4^{20} 0.999, n_D^{20} 1.5728, acetyl derivative, b.p. 109°) and 2 g of unaltered o-cresol. The yield of o-toluidine was 62.11%, on the basis of the amount of o-cresol taken, or 73.5% on the basis of the amount of o-cresol reacting.

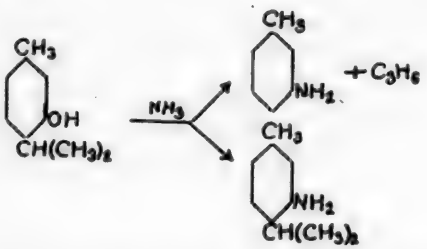
TABLE 2

Relation of the Aniline Yield to the Reaction Temperature

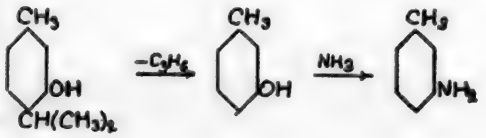
Quantity of phenol (g)	Ammonia pressure (atm)	Temperature of expt.	Rate of passage of phenol (drops per min)	Yield (g)		Aniline yield (%) based on phenol	
				aniline	phenol	taken	reacting
13	9.5	475°	6	10.2	0.2	79.3	88.3
18	8.5	450	6	7.0	9.0	39.3	78.6
18	8.5	400	8	7.0	9.0	39.3	83.3
23	8.5	300	8	0.9	21.3	3.9	63.6

Similar results were also obtained for the amination of p-cresol. By the amination of m-xylenol at 475°, at an ammonia pressure of 7 atm, and a rate of passage of m-xylenol of 8 drops per minute, we obtained m-xylidene in a yield of 40.3%, on the basis of the amount of m-xylenol taken, or 63% on the basis of the amount of m-xylenol reacting.

Interesting data were obtained by the amination of thymol. Thus, we obtained 10 g of amines by amination of 23 g of thymol at 475°, at a rate of passage of 10 drops per minute, and at an ammonia pressure of 10 atm. The following results were obtained by fractionally distilling the amines: 1st fraction, to 200°, 1.5 g; 2nd fraction, 200-204°, 7.0 g (d_4^{20} 0.9864 and n_D^{20} 1.5700); 3rd fraction, 204-240°, 1.0 g. For the product of the 2nd fraction, we obtained an acetyl and a phthalic derivative, which corresponded to these derivatives of m-toluidine. The formation of propylene was observed during the amination of thymol. From several experiments, we obtained 6 g of a fraction with a b.p. of 220-230°, in which the presence of thymylamine was observed via the acetyl derivative. Thus, apparently, the amination of thymol proceeds simultaneously in two directions:



It was of interest to elucidate the mechanism of the reaction, since the formation of m-toluidine as the result of two different reactions is possible. In the first place, under the conditions of the reaction, thymol may split off the isopropyl group as propylene, and the m-cresol which forms may be further converted to m-toluidine.



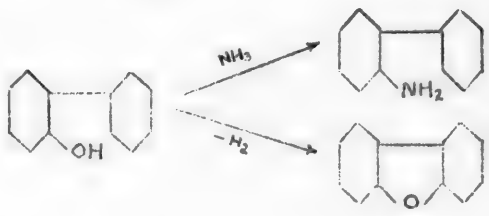
As is known, A. N. Engelgardt and P. Lachinov [6] found that thymol is converted to m-cresol by heating it with phosphoric anhydride.

We heated thymol to 475° with aluminum oxide (without ammonia), and observed the formation of a large quantity of m-cresol and the evolution of propylene. Therefore, this reaction may account for the formation of m-toluidine under our reaction conditions. At the same time, under the experimental conditions of the amination of thymol, we aminated 6 g of a fraction of amines, with a b.p. of 220-230°, which contained thymylamine. The formation of a gas of an unsaturated nature was also observed. The catalyzate obtained distilled over completely at 200-205°, and proved to be m-toluidine. Thus, m-toluidine can be formed from thymylamine under the conditions of our experiment.

Finally, it is very likely that both of these reactions proceed simultaneously and are the source of the formation of m-toluidine.

On amination of o-hydroxydiphenyl, two substances were found in the reaction products: o-aminodiphenyl and a product with a m.p. of 86-88°, diphenylene oxide, which was obtained in a predominating quantity. The latter formed a picrate with a m.p. of 93-94°.

Therefore, under the conditions of the experiment, both the amination of o-hydroxydiphenyl to o-aminodiphenyl, and its dehydrogenation to diphenylene oxide occur.



SUMMARY

The catalytic amination of monatomic phenols with compressed ammonia was studied. As the catalyst, we tested commercial active aluminum oxide.

By the amination of phenol, o- and p-cresols, and m-xylenol, the corresponding primary aromatic amines were formed in yields up to 88.0%.

m-Toluidine was obtained as the main product of the amination of thymol. This reaction may be considered as a new method for obtaining m-toluidine.

Both o-aminodiphenyl and diphenylene oxide were formed by the amination of o-hydroxydiphenol.

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SYNTHESIS OF Ar_2PbX_2 COMPOUNDS

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For the synthesis of the $ArPbX_3$ compounds [1], which we obtained for the first time (where Ar is the aromatic radical, and X is the organic acid group), we used Ar_2PbX_2 as the most convenient starting material. The synthesis of the latter was based partially on the arylation reaction of the organic salts of quadrivalent lead. Thus, by the method of Kocheshkov and Nad [2],

$$2Ar_2Hg + Pb(OOCCH_3)_4 \rightarrow Ar_2Pb(OOCCH_3)_2 + 2ArHgOOCCH_3$$

we obtained lead-organic compounds of the Ar_2PbX_2 class, which contained a substituent in the aromatic nucleus.

In the present article we have described the application of the method to the special case of dearylation by mercury salts:

$$Ar_4Pb + 2Hg(OOCCH_3)_2 \rightarrow Ar_2Pb(OOCCH_3)_2 + 2ArHgOOCCH_3$$

and have also improved the method of dearylation by organic acids, found by Polis [3] to be of most practical value

$$Ar_4Pb + 2RCOOH \rightarrow Ar_2Pb(OOCR)_2 + 2ArH.$$

Koton [4], developing the method of Polis, of the action of organic acids on completely substituted lead-organic compounds, treated the reaction products with water. We considered it expedient to carry out the treatment with organic solvents (gasoline), in order to avoid hydrolysis.

Finally, we were interested in overcoming some difficulties related to the direct dearylation by acids (for example, stearic acid), using the reacylation reaction:

$$(C_6H_5)_2Pb(OOCR)_2 + R'COOH \rightarrow (C_6H_5)_2Pb(OOCR')_2 + 2RCOOH.$$

According to our data, for example, the diacetate, dipropionate, and diisobutyrate of diphenyl lead, which are readily soluble in alcohol, enter into exchange reactions with acids, with the formation of less soluble salts. By this method we obtained diphenyl lead dibenzoate (m.p. 240°; according to Koton, m.p. of 231-232°), diphenyl lead distearate, diphenyl lead dimethacrylate and diphenyl lead dimonochloroacetate.

EXPERIMENTAL

Synthesis of diphenyl lead acetate by dearylation of lead tetraphenyl by mercuric acetate. In a flask fitted with a mechanical stirrer, we placed a solution of 1.03 g (1 mole) of lead tetraphenyl in 45 ml of chloroform, acidified it with 0.5 ml of acetic acid, and at room temperature added 1.28 g (2 moles) of mercuric acetate in portions, which gradually dissolved. After addition of the latter, the mixture was stirred for 1.5 hours more, the reaction mixture was transferred to a porcelain dish, and left in the air until the chloroform was removed, and then it was placed in a vacuum-desiccator over solid alkali, in order to remove acetic acid and possible traces of moisture. The residue was dissolved in 8 ml of boiling anhydrous alcohol, and the solution was cooled with a mixture of ice and salt. The precipitate was filtered off. The yield was 1 g (77.6%). The m.p. was 149° (for phenyl mercury acetate the m.p. was 149° [5]).

The alcohol was removed from the filtrate by evaporation in a vacuum-desiccator, and the residue with a m.p. of 195° was recrystallized from benzene acidified with a few drops of acetic acid. The yield was 0.6 g (62%). The m.p. was 200-201.5°. A mixture of a test sample and diphenyl lead diacetate obtained by a different method [4] showed no depression of the melting point.

Synthesis of diphenyl lead diisobutyrate. 1) To a solution of 1.03 g (1 mole) of lead tetraphenyl in 45 ml of chloroform, acidified with 0.78 g (4 moles plus 10% excess) of isobutyric acid, we gradually added 0.86 g (2 moles) of yellow mercuric oxide. After the latter dissolved, the solution was stirred for 2 hours longer. The solution was filtered to remove the slight turbidity, and left in the air until the chloroform had evaporated. The residue (2.3 g) was recrystallized from a hot mixture of benzene and ligroin, and had a m.p. of 204°. The diphenyl lead diisobutyrate melted at 204-205° (see below). A mixture of the substances showed no melting point depression.

2) In a three-necked flask fitted with a thermometer and a mechanical stirrer, we placed 20.6 g (1 mole) of lead tetraphenyl and 35 g (10 moles) of isobutyric acid. The mixture was heated at 115-120°. The residue of lead tetraphenyl dissolved after 25 minutes, after which the solution was stirred for 1.5 hours more at the same temperature. We added 60 ml of gasoline (the 75-100° fraction) to the hot reaction mass. A white, crystalline precipitate of pure diphenyl lead diisobutyrate came down. The yield was 15.3-17.6 g (72-84%). The m.p. was 203.5-204.5°. The melting point increased to 204-205° after recrystallization from hot benzene or from a mixture of benzene and ligroin.

0.2517 g sub.: 0.1419 g $PbSO_4$. 0.4304 g sub.: 0.2437 g $PbSO_4$. Found %: Pb 38.51, 38.66. $C_{20}H_{24}O_4Pb$. Calculated %: Pb 38.70.

The diphenyl lead diisobutyrate consisted of snow-white needles with a m.p. of 204-205°. It dissolved readily in the cold in dichlorethane and acetic acid; it dissolved moderately in the cold, and well on heating, in benzene, xylene and chloroform; it did not dissolved in the cold, but dissolved moderately on heating, in ligroin; it dissolved very poorly in ether and petroleum ether, even on heating.

Synthesis of diphenyl lead dipropionate. 20.6 g (1 mole) of lead tetraphenyl and 29.6 g (10 moles) of propionic acid were heated at 110-115°, and stirred mechanically. The lead tetraphenyl dissolved after 15 minutes. The mixture was heated for 1.5 hours more at the same temperature. We poured 120 ml of gasoline (75-100° fraction) into the hot solution. Crystallization began immediately. On the following day, the precipitate was filtered off, washed with gasoline and dried in vacuo at 61° (heating by chloroform vapors). The yield of crude product was 11.2 g (55%). The m.p. was 181.5-182.5°, which did not change on repeated crystallization. Diphenyl lead dipropionate, according to Koton [4] had a m.p. of 170-172°.

0.1783 g sub.: 0.1073 g $PbSO_4$. 0.2128 g sub.: 0.1272 g $PbSO_4$. Found %: Pb 41.12, 40.84. $C_{18}H_{20}O_4Pb$. Calculated %: Pb 40.84.

Diphenyl lead dipropionate was a white crystalline substance. It dissolved very well in alcohol and acetone, and well in ethyl acetate, benzene, and chloroform in the cold; it dissolved moderately in carbon tetrachloride in the cold, and well on heating; and it dissolved poorly in ether and ligroin, even on heating.

Synthesis of diphenyl lead distearate. 2.68 g (1 mole) of diphenyl lead diisobutyrate was dissolved at 35° in 22 ml of anhydrous alcohol; 2.84 g (2 moles) of stearic acid was dissolved at the same temperature in 95 ml of anhydrous alcohol. The solutions were poured together and, in order not to crystallize out the stearic acid, the mixture was maintained at 35°. Crystals of diphenyl lead distearate gradually separated from the solution. Since crystallization was completed only from a warm solution, it was kept at room temperature for several hours. The stearic acid which partially precipitated was brought back into solution by heating the reaction mixture to 40°, thus quickly clarifying the solution. The precipitate was washed with alcohol. We obtained 2.95 g (64.1%) of product. The m.p. was 98-99°. The precipitate was recrystallized from 50 ml of anhydrous alcohol and washed with warm anhydrous alcohol. The yield was 2.3 g, and the m.p. was 100-101°.

0.2346 g sub.: 0.0775 g $PbSO_4$. 0.2031 g sub.: 0.0660 g $PbSO_4$. Found %: Pb 22.56, 22.20. $C_{46}H_{80}O_4Pb$. Calculated %: Pb 22.30.

In external form the diphenyl lead distearate was similar to stearic acid. It dissolved very well in the cold in chloroform and in benzene; it dissolved moderately in ligroin in the cold, and well on heating; it did not dissolve in alcohol and acetone in the cold, but on heating it dissolved moderately; it did not dissolve in ether in the cold, but was moderately soluble on heating.

Diphenyl lead distearate could be obtained also by heating a solution of diphenyl lead diacetate in molten stearic acid (at 120-140°) in vacuo. The acetic acid was removed, and the remaining mixture of diphenyl lead distearate and stearic acid was recrystallized from alcohol or ether. In this case, the separation from stearic acid, which was found to be in excess, was less convenient.

Synthesis of diphenyl lead dibenzoate. 2.14 g (1 mole) of diphenyl lead diisobutyrate was dissolved in 15 ml of hot anhydrous alcohol. 1.1 g (2 moles plus 10% excess) of benzoic acid was dissolved in 3 ml of anhydrous alcohol. The solutions were poured together hot. Crystallization of the dibenzoate began after several minutes. The precipitate was filtered off, washed with alcohol, and dried as usual in vacuo. We obtained 2 g (83%) of crude product with a m.p. of 227-230°. After recrystallization from 100 ml of dry benzene, the m.p. was 240°, and it did not change on further crystallization. The yield was 1.25 g.

0.2002 g sub.: 0.1005 g $PbSO_4$. 0.2428 g sub.: 0.1220 g $PbSO_4$. Found %: Pb 34.30, 34.33. $C_{26}H_{20}O_4Pb$. Calculated %: Pb 34.34.

Diphenyl lead dibenzoate, obtained in a yield of 35% according to Koton [4], by the direct action of benzoic acid on lead tetraphenyl, had a m.p. of 231-232°, but the substance he obtained differed by 0.71% in lead content from that calculated.

Diphenyl lead dibenzoate dissolved well in the cold in ethyl acetate and chloroform; it dissolved poorly in the cold, and moderately on heating in alcohol, acetone and benzene; it did not dissolve in ether, hexane and water.

Synthesis of diphenyl lead dimethacrylate. Into a solution of 0.45 g (1 mole) of diphenyl lead diisobutyrate in 4.5 ml of anhydrous alcohol we poured 0.2 g (2 moles plus 35% excess) of methacrylic acid. A finely-crystalline precipitate appeared immediately, and after half an hour it was filtered off, washed with alcohol, and dried as usual in vacuo. The yield was 0.43 g (96%). The substance turned yellow on heating in a capillary at 205°, and decomposed at 212° without melting. Diphenyl lead dimethacrylate dissolved moderately on heating in chloroform, acrylic acid, styrene and amylene; it dissolved poorly in alcohol, acetone and ethyl acetate, and very poorly in benzene; it did not dissolve in ether and hexane.

0.1272 g sub.: 0.0722 g $PbSO_4$. Found %: Pb 38.78. $C_{22}H_{22}O_4Pb$. Calculated %: Pb 39.00.

On repeating the experiment, using diphenyl lead dipropionate as the starting material, we obtained a 90% yield of the same compound.

0.1576 g sub.: 0.905 g $PbSO_4$. Found %: Pb 39.23.

Synthesis of diphenyl lead dimonochloroacetate. 2.67 g (1 mole) of diphenyl lead diisobutyrate was dissolved by heating it slightly in 15 ml alcohol; 1.9 g (4 moles) of monochloroacetic acid was dissolved in 2 ml of warmed alcohol. The solutions were mixed. Crystallization began immediately. The precipitate was filtered off, washed with alcohol and dried in vacuo. The yield was 2.16 g (77.5%).

0.3046 g sub.: 0.1677 g $PbSO_4$. 0.2299 g sub.: 0.1276 g $PbSO_4$. 0.1995 g sub.: 7.27 ml 0.1 N $AgNO_3$. Found %: Pb 37.62, 37.92; Cl 12.92. $C_{16}H_{14}O_4Cl_2Pb$. Calculated %: Pb 37.79; Cl 12.92.

The diphenyl lead dimonochloroacetate consisted of white needles, which, when heated in a capillary at 185-205°, gradually decomposed without melting. The substance dissolved poorly in alcohol, acetone, and chloroform in the cold, and moderately on heating; it did not dissolve in benzene in the cold, and dissolved poorly on heating; it did not dissolve in ether and hexane, even on heating.

SUMMARY

1. It was shown that the reaction of the dearylation of Ar_4Pb compounds by the mercuric salts of organic acids may be utilized for the synthesis of lead-organic salts of the $Ar_2Pb(OOCR)_2$ type.

2. We simplified the method of synthesis of lead-organic salts of the $Ar_2Pb(OOCR)_2$ type involving the dearylation of Ar_4Pb by organic acids.

3. The reacylation reaction was used for the synthesis of lead-organic salts of the $Ar_2Pb(OOCR)_2$ type, which were difficultly available by other methods.

4. For the first time, the diisobutyrate, dimethacrylate, distearate and dimonochloroacetate of diphenyl lead were described.

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THERMAL DECOMPOSITION OF BENZOYL PEROXIDE IN MIXTURES OF SOLVENTS – BENZENE AND METHYL ALCOHOL, CARBON TETRACHLORIDE AND ISOPROPYL ALCOHOL

B. N. Moryganov

In the study of free-radical reactions in solutions with mixtures of different solvents, it is possible to establish the relative reactivity of the radicals with different components of the mixtures. An especially large number of works in this field relate to investigations of the reactions of benzoyl peroxide in mixtures of different aromatic compounds [1].

Rafikov and Kudinova studied the reaction of benzoyl peroxide with a mixture of benzene and ethyl alcohol [2]. We previously studied the reaction of benzoyl peroxide with alcohols, whereby the great ease of interaction of benzoyl peroxide with methyl alcohol [3] was noted. It seemed to us to be of interest to study the reaction of benzoyl peroxide in a mixture of benzene and methyl alcohol. The results obtained from the investigation agreed completely with the ideas which were developed in the work [2]. Reaction proceeded to a great degree between benzoyl peroxide and methyl alcohol. However, in spite of the fact that the reaction between the alcohol and benzoyl peroxide proceeds also more easily at lower temperatures, in our experiments we also definitely demonstrated the reaction of benzoyl peroxide with benzene, which could be judged from the formation of diphenyl (in a quantity up to 0.14 mole per 1 mole of peroxide). Only traces of diphenyl were observed in experiments on the reaction of the peroxide with alcohols. In our experiments we observed a shift of the equilibrium, just as noted also in the work [2], which the authors accounted for by the fact that benzene also was formed during the decomposition of benzoyl peroxide.

The problem remains confused as to whether the phenyl radicals which form from benzene as a result of the chain reaction with the peroxide, react with the alcohol. If such a reaction should occur then we might not detect it, since the products obtained would be the same as in the absence of this reaction. Solution of this problem might be obtained only by the use of deuterorated compounds in the reactions studied. We succeeded in rigorously demonstrating the interaction of the free radicals formed by the reaction of carbon tetrachloride with methyl alcohol [3]. In the present work, we examined the possibility of such a reaction with other alcohols, and for this isopropyl alcohol was chosen. In this case, we observed the interaction of benzoyl peroxide with both components of the mixture. The formation of phthalic acid and hexachloroethane was demonstrated as due to the reaction of carbon tetrachloride. The benzoic acid and acetone formed indicated that the alcohol and the benzoyl peroxide reacted. It should be noted that the secondary free radicals which formed from the solvents, reacted, which can be judged from the evolution of hydrogen chloride and the formation of chloroform.

EXPERIMENTAL

Thermal Decomposition Reaction of Benzoyl Peroxide in a Mixture of Benzene and Methyl Alcohol

The reaction mixture was heated on a water bath for 40 hours in a round-bottomed flask with a reflux ball condenser. In each experiment 6 g of benzoyl peroxide was decomposed in equimolecular quantities of methyl alcohol (32 g) and benzene (78 g). Moreover, experiments were conducted with 50 g of benzoyl peroxide and with the quantities of solvents cited above. The yields of the products of the reaction, made with different quantities of peroxide, were similar, especially as to the yields of benzoic acid. Carbon dioxide was absorbed in traps containing 40% solutions of potassium hydroxide. 0.46 mole of CO_2 per 1 mole of benzoylperoxide decomposing was absorbed. Fine, white crystals were formed by heating the reaction mixture in a flask and also in sealed tubes, but because of their small quantity they were not studied. The crystals were separated, the liquid portion of the reaction products was distilled, and the fraction which distilled at a b.p. of 56-78.5° was diluted with water. We determined formaldehyde, in a quantity of 0.28 mole per 1 mole of peroxide decomposing, in the water-alcohol solution by precipitation of the dimedon derivative. A mixture of the dimedon derivative of formaldehyde produced and a test sample melted at 186°.

Methylal was not observed in the water-alcohol solution after heating with dilute hydrochloric acid (in a flask with a reflux condenser).

After removal of the fraction with the b.p. of 56-78.5° the residuals were alkalized and steam-distilled. Diphenyl with a m.p. of 68-69° was isolated in a quantity of 0.14 mole per 1 mole of benzoyl peroxide decomposing; a mixture of a test sample and known substance gave no m.p. depression. On completion of the steam distillation,

the alkaline solution from the distillation flask was separated from the small quantity of resins which formed, and acidified with dilute hydrochloric acid. Benzoic acid, m.p. 121°, separated, and a mixture of a test sample and the known substance gave no depression. By titration with a 0.5 N solution of alkali we determined benzoic acid in the quantity of 1.02 moles per 1 mole of benzoyl peroxide decomposing. The presence of phenyl benzoate in the residue from the distillation could be expected, but we were unable to detect it.

Similar results were obtained, and very similar yields of products were obtained, as a result of the decomposition of benzoyl peroxide in a mixture of benzene and methyl alcohol, by heating in sealed tubes at 150° for 20 hours.

Thermal Decomposition Reaction of Benzoyl Peroxide in a Mixture of Carbon Tetrachloride and Isopropyl Alcohol

A reaction mixture consisting of equimolecular quantities of carbon tetrachloride (154 g) and isopropyl alcohol (60 g), and different quantities of benzoyl peroxide (0.25, 0.5, 1, 2, 3 and 6 g) in various experiments, was introduced into a flask with a ground-in reflux condenser connected to an absorber, and was heated on a water bath for 80 hours. The gases which formed during the reaction were absorbed: HCl was absorbed in distilled water, and CO_2 was absorbed in a saturated solution of barium hydroxide. The quantity of CO_2 (0.38-1.59 moles per 1 mole of peroxide decomposing) was determined gravimetrically.

The liquid products were acidic and were washed free of alcohol, acetone and HCl by distilled water until they were neutral. The quantity of HCl from the absorber and from the water-alcohol solution (5.27-39.72 moles per 1 mole of peroxide decomposing) was determined by titration with 0.1 or 0.5 N solutions of alkali. In the water-alcohol solution we determined acetone (4.68-34.31 moles per 1 mole of peroxide decomposing) as the 2,4-dinitrophenylhydrazone; the m.p. was 125°. A mixture of a test sample with the known substance showed no depression. The liquid reaction products were distilled after they were washed with water and dried with calcium chloride. A fraction with a b.p. of 65-76° (a mixture of chloroform and carbon tetrachloride) distilled. Chloroform (b.p. 60.5-62.5°, n_D^{20} 1.474 , d_4^{20} 1.4415) was separated by fractional distillation. After distillation of the fraction with a b.p. of 65-76°, the residuals were steam distilled. The distillate contained isopropyl benzoate and hexachloroethane. Benzoic acid, m.p. 121°, was separated after saponification of the ester from the acidified solution. A mixture of a test sample with the known substance gave no m.p. depression. The residue, after saponification of the ester, contained hexachloroethane, which was purified by volatilization with sulfuric acid. A mixture of purified hexachloroethane and a test sample melted at 186°. On completion of the distillation, the alkaline solution from the distillation flask was separated from the small quantity of resins produced, and acidified with dilute hydrochloric acid. Benzoic acid with a m.p. of 121° (from water) was separated. A mixture of a test sample gave no depression. The o-phthalic acid constituting the resin was identified with resorcinol by the fluorescein reaction.

SUMMARY

1. CO_2, benzoic acid methyl benzoate, formaldehyde and diphenyl were formed by the thermal decomposition of benzoyl peroxide in a mixture of benzene and methyl alcohol.

2. It was shown that, in the thermal decomposition of benzoyl peroxide in a mixture of benzene and methyl alcohol, reaction of the peroxide proceeds simultaneously with both components of the mixture. The interaction of the peroxide with the alcohol proceeds to the greater degree.

3. Hydrogen chloride, chloroform, acetone, CO_2, benzoic acid isopropyl benzoate, phthalic acid and hexachloroethane were formed by the thermal decomposition of benzoyl peroxide in a mixture of carbon tetrachloride and isopropyl alcohol.

4. It was shown that, besides the reaction between the carbon tetrachloride and isopropyl alcohol, which was initiated by the peroxide, reaction of the latter with both components of the mixture occurred during the heating of benzoyl peroxide in a mixture of carbon tetrachloride and isopropyl alcohol.

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CHAIN REACTIONS OF CARBON TETRACHLORIDE AND ALCOHOLS

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We recorded earlier that the reaction of carbon tetrachloride and isopropyl alcohol is initiated by benzoyl peroxide [1]. In the present work we have studied at greater length the chain reaction initiated by benzoyl peroxide between carbon tetrachloride and alcohols (methyl alcohol and isopropyl alcohol). The reaction takes place with the formation of HCl, $CHCl_3$, and an aldehyde or a ketone. Determination of the length of the chain is most conveniently made from the yield of HCl. For determination of the chain length in the system, carbon tetrachloride – isopropyl alcohol, the quantity of acetone formed may also be used. In both cases the results that we obtained agreed satisfactorily. It was difficult to determine chloroform quantitatively, therefore, we were restricted to its identification without a quantitative calculation.

TABLE 1

Chain Reaction of Carbon Tetrachloride and Isopropyl Alcohol, Initiated by Benzoyl Peroxide

Test No.	Quantity of benzoyl peroxide (moles) reaction products	0.0248 in moles per 1 mole of peroxide decomposed	0.0124 in moles per 1 mole of peroxide decomposed	0.0083 in moles per 1 mole of peroxide decomposed	0.0041 in moles per 1 mole of peroxide decomposed	0.0021 in moles per 1 mole of peroxide decomposed	0.0010 in moles per 1 mole of peroxide decomposed
1	HCl	5.27	5.65	9.90	13.95	22.95	39.72
2	CH_3COCH_3	4.68	5.95	9.35	17.46	27.90	34.31
3	CO_2	0.38	0.42	0.58	0.99	1.30	1.59

Blank experiments conducted by heating carbon tetrachloride with alcohols showed that, although reaction occurs between them without benzoyl peroxide, with the separation of HCl, the quantitative yield of the products is very small in comparison with that from reactions conducted with the peroxide. The appropriate corrections for the quantities of HCl and acetone formed by this reaction were introduced into the data cited in the tables. The results obtained

TABLE 2

Chain Reaction of Carbon Tetrachloride and Methyl Alcohol, Initiated by Benzoyl Peroxide

Test No.	Quantity of benzoyl peroxide (moles) reaction products	0.0248 in moles per 1 mole of peroxide decomposed	0.0083 in moles per 1 mole of peroxide decomposed	0.0041 in moles per 1 mole of peroxide decomposed	0.0021 in moles per 1 mole of peroxide decomposed	0.0010 in moles per 1 mole of peroxide decomposed
1	HCl	1.39	1.44	1.73	2.38	4.30
2	CO_2	0.32	0.41	0.61	0.76	0.90

are recorded in Tables 1 and 2. It should be noted that the amount of CO_2 which evolved varied with the benzoyl peroxide concentration; the quantity of CO_2 increases with a decrease of the peroxide concentration, whereupon the increase of the CO_2 yield was much greater for isopropyl alcohol than for methyl alcohol.

On the basis of the reactions and the investigations of the interaction of carbon tetrachloride with alcohols, which we conducted earlier by heating and by exposure to ultraviolet light [2], the mechanism of the process between benzoyl peroxide and alcohols can be represented as follows:

1. Initiation:

$$(C_6H_5COO)_2 \rightarrow 2C_6H_5COO\cdot$$

$$C_6H_5COO\cdot \rightarrow C_6H_5\cdot + CO_2$$

2. Beginning of chains:

$$C_6H_5COO\cdot + CH_3CHOHCH_3 \rightarrow C_6H_5COOH + \dot{C}H_3COHCH_3$$

$$C_6H_5\cdot + CH_3CHOHCH_3 \rightarrow C_6H_6 + CH_3\dot{C}OHCH_3$$

or

$$C_6H_5\cdot + CCl_4 \rightarrow C_6H_5Cl + CCl_3\cdot$$

3. Chain:

$$CH_3\dot{C}OHCH_3 + CCl_4 \rightarrow CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2 + CCl_3\cdot$$

$$CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2 + HCl$$

$$CH_3-CHOH-CH_2 + CCl_3\cdot \rightarrow CHCl_3 + CH_3\dot{C}OHCH_3, \text{ etc.}$$

4. Breaking of chain:

a) $2CCl_3\cdot \rightarrow C_2Cl_6$

b) $2CH_3\dot{C}OHCH_3 \rightarrow CH_3CHOHCH_3 + CH_3COCH_3$

The reaction of carbon tetrachloride with methyl alcohol, initiated by benzoyl peroxide, proceeds similarly, but the chain length is much shorter.

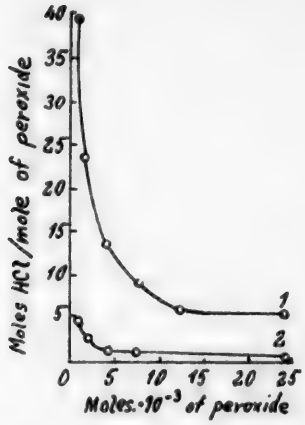
It is interesting to compare the chain lengths in terms of the amount of HCl liberated from the quantity of benzoyl peroxide taken. These relations are presented for isopropyl and methyl alcohols by curves in the Figure. In both cases a sharp increase of the chain lengths with a decrease of the peroxide concentration is evident. Nevertheless, under the conditions that we described, the chain lengths are much shorter for methyl alcohol.

EXPERIMENTAL

Reaction of carbon tetrachloride with isopropyl alcohol in the presence of benzoyl peroxide. Into a flask with a ground-in reflux condenser connected to absorbers for HCl and CO_2, 154 g (1 mole) of CCl_4, 60 g (1 mole) of isopropyl alcohol, and different (in different experiments) quantities of benzoyl peroxide (0.25, 0.5, 1, 2, 3 and 6 g) were charged. The reaction mixture was heated on the water bath for 80 hours. The length of time of heating was determined by the time of the disappearance of the peroxide. The reaction was stopped when traces of peroxide remained in the reaction mixture, for which about 80 hours were usually required. This time was taken for all the experiments. The gases which formed during the reaction were absorbed: HCl was absorbed in distilled water, and CO_2 was absorbed in a saturated solution of barium hydroxide. The liquid reaction products were washed with distilled water until they were neutral, in order to remove isopropyl alcohol and other water-soluble substances, particularly HCl. The HCl from the trap and from the water-alcohol solution was determined by titration with a 0.1 or 0.5 N solution of alkali. In the water-alcohol solution, acetone was determined as the 2,4-dinitrophenylhydrazone; its m.p. was 125°, and a test sample of a mixture showed no m.p. depression.

After a washing with water and a drying with calcium chloride, the liquid water-insoluble reaction products were distilled. A fraction with a b.p. of 65-76° (a mixture of chloroform and carbon tetrachloride) distilled. After an additional drying with calcium chloride, and then with P_2O_5, chloroform (b.p. 60.5-62.5°, d_4^{20} 1.474, n_D^{20} 1.4415) was separated from this fraction by fractional distillation. The benzoyl peroxide decomposition products were not investigated in the present work, since we determined them earlier in experiments with isopropyl alcohol [3].

Blank experiments, without benzoyl peroxide, were made for CCl_4 and isopropyl alcohol, from which after an 80-hour heating we obtained 0.42 g of HCl and 0.09 g of acetone. The appropriate corrections were introduced into the tables.



Relation of chain lengths to the benzoyl peroxide concentration. 1) CCl_4 + isopropyl alcohol; 2) CCl_4 + methyl alcohol.

Reaction of carbon tetrachloride and methyl alcohol in the presence of benzoyl peroxide. In different experiments we introduced different quantities of benzoyl peroxide (0.25, 0.5, 1, 2, and 6 g) into equimolecular quantities of carbon tetrachloride (154 g) and methyl alcohol (32 g). The components were heated on the water bath for 40 hours. After this time no more peroxide remained in the reaction mixture. The gases which formed were absorbed by distilled water (HCl) and by a saturated solution of barium hydroxide (CO_2). The liquid reaction products were acidic, and the alcohol, other water-soluble substances and HCl were washed out with distilled water until the reaction products were neutral. The HCl from the absorbers and from the water-alcohol solution was determined by titration with a 0.1 N solution of alkali. Formaldehyde was determined in the acidic water-alcohol solution as the dimedon derivative precipitate (m.p. 186°, test sample of mixture).

After a washing with water and a drying with calcium chloride, the liquid reaction products were distilled. A fraction with a b.p. of 70-76° distilled. This fraction was refluxed with dilute hydrochloric acid in order to break methylal down to the alcohol and formaldehyde; after a drying over P_2O_5, the refluxed solution was fractionally distilled, and a chloroform fraction was separated (b.p. 61-63°, d_4^{20} 1.4950, n_D^{20} 1.4450). The benzoyl peroxide decomposition products were isolated earlier [4].

As also in the preceding work, blank experiments were carried out, and corrections were made for HCl, and were recorded in Table 2. (Quantity of HCl in all tests, 0.01 g).

SUMMARY

1. It was shown that benzoyl peroxide initiates a chain reaction between carbon tetrachloride and methyl or isopropyl alcohol.

2. It was found that the length of the chain is much longer in the reactions with isopropyl alcohol.

3. A mechanism was proposed for the chain reaction between carbon tetrachloride and alcohols.

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THE PROBLEM OF THE STUDY OF THE REACTION MECHANISM OF THE ESTERIFICATION OF ETHYL ALCOHOL OVER COPPER CATALYSTS

IV. CONSECUTIVE CONVERSIONS OF ALCOHOL TO ACETALDEHYDE AND ETHYL ACETATE ACCORDING TO THE LENGTH OF THE CATALYST LAYER

B. N. Dolgov, T. V. Nizovkina and I. M. Stroiman

During a study of the catalytic reaction of the formation of ethyl acetate from mixtures of ethyl alcohol and acetaldehyde, we found [1] that ethyl acetate is produced from such mixtures in an amount which exceeds the quantity of alcohol reacted, and that part of the ethyl acetate forms from the acetaldehyde. We expressed the assumption that even in the esterification of pure ethyl alcohol over copper catalysts, acetaldehyde is an intermediate reaction product. Additional data which confirm the validity of this assumption are cited in the present work. These data were obtained as a result of experiments on the study of the variations of acetaldehyde and ethyl acetate yields in relation to the length of the catalyst layer in the esterification of ethyl alcohol.

We used a copper-activated catalyst for carrying out the dehydrogenation and esterification reactions of ethyl alcohol. The catalyst was active with respect to both the dehydrogenation and the esterification reactions, thanks to which we always found acetaldehyde and ethyl acetate in the reaction products in quantities which enabled us to establish accurately the ratios between them.

Alcohol vapors were passed through a reactor, into which a definite quantity of catalyst was charged. The yields of the reaction products were studied for three different lengths of catalyst layer. In the first series of experiments 5.5 ml of the catalyst was placed in the reactor, in the second series – 11 ml, and in the third – 22 ml. The reactor was placed in an oil thermostat in order to provide constant temperatures. Experiments were carried out at 220 and 240°. Fluctuations of the temperatures did not exceed 0.5°. For each temperature and each catalyst layer taken, we carried out 4 experiments at different volume rates, corresponding to inputs of 0.032, 0.064, 0.128 and 0.160 g of alcohol per minute.

The apparatus and the analysis of the products were described in [1].

The results of the experiments are cited in Table 1.

The effect of variation of the length of the catalyst layer on the yield of reaction products may be seen in Figs. 1, 2 and 3. The change of the alcohol quantity is shown in Fig. 1. The slope of the curves indicates that the quantity of alcohol decreases sharply on passage over a layer comprising 5.5 ml of catalyst, it continues to decrease on passage through the next 5.5 ml of catalyst, but changes little with a further increase of the catalyst layer to 22 ml.

The acetaldehyde content, as shown by the slope of the curves in Fig. 2, increases on passage over the first 5.5 ml of catalyst, reaches a maximum in the region of the second 5.5 ml, and decreases sharply with passage over the last 11 ml of catalyst.

According to Fig. 3, the ethyl acetate content in the reaction products increases in direct proportion to the increase of the length of the catalyst layer, for which the most rapid increase of the ethyl acetate content was observed within the range of the second catalyst layer – from 5.5 to 11 ml.

A comparison of these results shows that on passage over the last 11 ml of catalyst the increase in the ethyl acetate yield can result only from the acetaldehyde, and not from the alcohol, the quantity of which scarcely varied in this layer. In the preceding catalyst layers, the rate of formation of ethyl acetate varied concurrently with the change of the acetaldehyde concentration, but showed an inverse relationship to the alcohol concentration; in the second catalyst layer, the rate of formation of the ester was greater than in the first, while the alcohol content in the second layer was much lower (by some ten per cent) than in the first. These data confirmed our assumption that the esterification reaction of ethyl alcohol to ethyl acetate is a consecutive reaction, and that the first stage of the reaction consists of the formation of an intermediate product – acetaldehyde, from which the formation of ethyl acetate occurs.

TABLE 1

Experiments with Alcohol over Different Catalyst Layers (alcohol 95.5% by wt., d_4^{20} 0.8087)

Temperature	Length of time of expt. (min)	Quantity of alcohol supplied (g/min)	Obtained in the expt. liquid condensate (g)	Obtained in the expt. gas under standard conditions (ml)	Liquid products obtained (in percents by wt. of condensate) acetic acid	ethyl acetate	acetaldehyde	ethyl alcoinol
			Volume of catalyst 5.5 ml					
220°	60	0.032	1.84	194	0.1	7.7	8.3	77.5
220	30	0.064	1.84	128	0.2	5.6	6.4	81.7
220	30	0.128	3.92	194	0.1	4.0	7.8	82.1
220	30	0.160	4.60	270	0.1	3.7	6.8	83.4
240	60	0.032	1.84	288	0.3	11.4	12.4	69.5
240	30	0.064	1.86	217	0.2	9.1	11.8	72.6
240	30	0.128	3.80	568	0.14	6.7	10.6	76.3
240	30	0.160	5.50	405	0.13	5.5	10.0	79.0
			Volume of catalyst 11 ml					
220	60	0.032	1.87	288	0.50	20.4	8.4	64.3
220	30	0.064	1.76	233	0.40	17.1	9.5	66.3
220	30	0.128	3.51	393	0.30	13.0	9.2	77.3
220	30	0.160	4.60	557	0.30	12.1	9.7	71.5
240	60	0.032	1.74	453	0.90	29.6	11.8	–
240	30	0.064	2.12	486	0.70	26.2	11.3	80.7
240	30	0.128	3.71	716	0.47	20.6	13.5	59.0
240	30	0.160	4.58	844	0.44	19.0	13.1	60.9
			Volume of catalyst 22 ml					
220	60	0.032	1.74	595	0.77	27.0	5.9	65.3
220	30	0.064	2.05	376	0.52	23.0	5.2	64.9
220	30	0.128	3.96	634	0.33	18.8	7.7	67.0
220	30	0.160	4.76	743	0.33	17.3	8.4	67.7
240	60	0.032	1.84	469	0.54	30.0	4.3	68.5
240	30	0.064	1.84	446	1.0	30.0	6.7	55.9
240	30	0.128	3.60	734	0.88	27.8	8.3	57.0
240	30	0.160	4.60	816	0.80	27.3	8.8	56.5

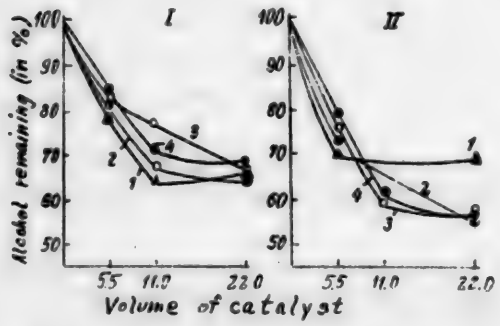

Fig. 1 Effect of the length of the catalyst layer on the yield of reaction products. I) 220°; II) 240°. Input: 1) 0.032 g/min; 2) 0.064 g/min; 3) 0.128 g/min; 4) 0.160 g/min.

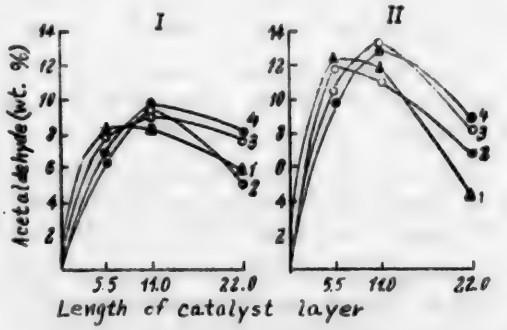

Fig. 2. Relation of the acetaldehyde yield (in wt. %) to the length of the catalyst layer. I) 220°; II) 240°. Input: 1) 0.032 g/min; 2) 0.064 g/min; 3) 0.128 g/min; 4) 0.160 g/min.

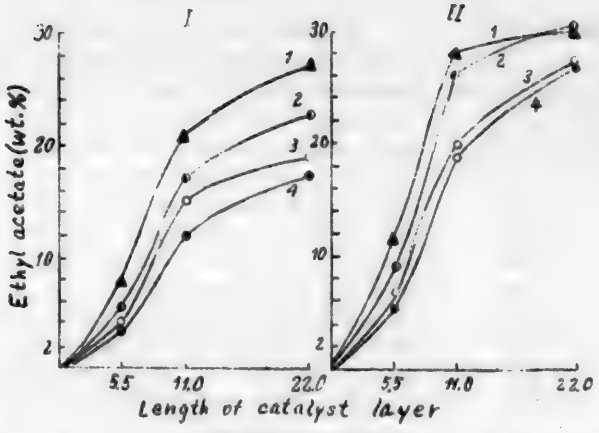

Fig. 3 Relation of the ethyl acetate yield (in wt. %) to the length of the catalyst layer. I) 220°; II) 240°. Input: 1) 0.032 g/min; 2) 0.064 g/min; 3) 0.128 g/min; 4) 0.160 g/min.

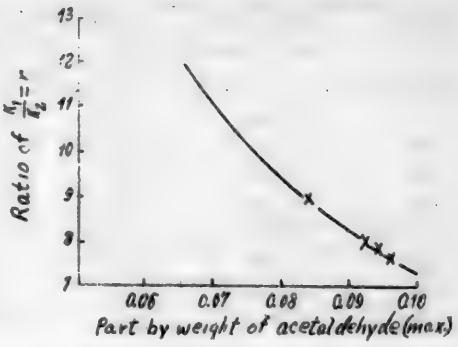

Fig. 4. Relation of the value of r to the part by weight of acetaldehyde.

The rate of the consecutive reaction which we considered depends on diffusion, as we showed earlier, but it also depends on the concentration of reactants on the catalyst surface. Since the adsorption coefficients of ethyl acetate and acetaldehyde are close together, the rate equation of this consecutive reaction does not depend sharply on the denominator in the formula of the Langmuir adsorption isotherm, and can be assumed to be approximately an expression of a first order reaction. The ratio between the aldehyde and ethyl acetate may be evaluated, using the well-known derivation of the formulas of the kinetics of consecutive first order reactions [2]. The content of the final product, in our case ethyl acetate, in the reaction mixture at the moment t may be represented by the formula

$$y = a\left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t}\right), \quad (1)$$

where k_1 and k_2 are the rate constants of the dehydrogenation of alcohol to acetaldehyde, and the esterification of the acetaldehyde to ethyl acetate; y is the ethyl acetate content in the reaction mixture; a is the initial per cent by weight of the alcohol; and t is the period of passage of the reaction layer along a definite length of catalyst layer.

The quantity of intermediate product – acetaldehyde – at this same moment is expressed by the formula

$$x - y = \frac{k_1 a}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right), \quad (2)$$

where x is the portion of alcohol which had time to react at the moment t. The remaining symbols are the same as in equation (1).

The maximum yield of intermediate product may be expressed by the equation

$$(x-y)_{max} = \frac{a_2}{1-r}\left(e^{-r\frac{\ln r}{r-1}} - e^{-\frac{\ln r}{r-1}}\right), \quad (3)$$

where r is the ratio of both reaction rates, $\frac{k_1}{k_2}$ and $k_1 = k_2 r$.

Using equation (3), we calculated the ratio between both products from experimental data, proceeding from the maximum yield of acetaldehyde, taken from Fig. 2. We obtained a series of curves which indicated the yields of acetaldehyde in relation to the length of the catalyst layer, at different rates of input of alcohol. Nevertheless, for each rate of input that point is inadequate for judgment concerning the position of the maximum, however, the validity of the decrease of the maxima and the identity of the character and slope of the curves for different inputs, offers the possibility of determining the maximum acetaldehyde yield rather accurately. The results obtained are cited in Table 2 and in Fig 4, where the data obtained experimentally are plotted on the theoretically calculated curve.

TABLE 2

Calculation of the Ratio of the Rate Constants of the Reactions of Formation of Acetaldehyde and Ethyl Acetate

Temperature of experiment	Quantity of alcohol supplied	Time of contact (sec)	Maximum yield of acetaldehyde (part by weight)	Ratio of rate constants
220°	0.032	0.590	0.084	9.00
220	0.064	0.335	0.095	7.75
220	0.128	0.161	0.092	8.00
220	0.160	0.128	0.098	7.50
240	0.032	0.560	0.124	5.45
240	0.064	0.257	0.117	5.90
240	0.128	0.152	0.135	4.80
240	0.160	0.171	0.130	5.00

SUMMARY

It was shown that, in proportion to the passage over the length of the catalyst layer, the composition of the reaction products of the transformation of ethyl alcohol over a copper activated catalyst, vary in such a way that in the first layers of catalyst chiefly the formation of acetaldehyde occurs, which in the following layers is later converted to ethyl acetate. The maximum yield of ethyl acetate, corresponding to the passage over a definite length of catalyst, may serve as the characteristic activity of the catalyst with respect to the dehydrogenation reaction of the alcohol and the ester condensation of acetaldehyde.

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DERIVATIVES OF ACETYLENE

166. CYANOETHYLATION OF ACETYLENE ALCOHOLS

I. N. Nazarov and G. A. Shvekhgeimer

The present work is a continuation of our investigation [1] of the reaction of acetylene alcohols and acrylonitrile. In all the experiments a 40% aqueous solution of potassium hydroxide was used as the catalyst. In carrying out the reaction of acrylonitrile with the crystalline acetylene alcohols, dioxane which had not been subjected to preliminary purification from peroxide was used as the solvent, but before distillation the reaction mixture was stirred for 1 hour with a small quantity of ferrous sulfate.

On cyanoethylation of propylethynylcarbinol, an 82% yield of the corresponding β-cyanoethyl ether (I) was obtained.

(I)

The branching of the chain in isopropylethynylcarbinol did not appear to be a great hindrance to the cyanoethylation reaction, and a 61% yield of the corresponding β-cyanoethyl ether (II) formed:

(II)

The secondary acetylene alcohol (III), which has a benzene nucleus in its molecule, adds acrylonitrile smoothly, forming an 80% yield of the β-cyanoethyl ether (IV):

(III) (IV)

Tertiary acetylene alcohols, unlike their saturated analogs, also enter readily into the cyanoethylation reaction.

On reaction of methylethylethynylcarbinol with acrylonitrile, a 96% yield of the β-cyanoethyl ether (V) was obtained:

(V)

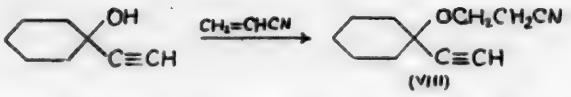
As is obvious from the reaction of dipropylethynylcarbinol with acrylonitrile, an increase of the radical in the tertiary acetylene alcohols did not affect this reaction; thus a 95% yield of β-cyanoethyl ether (VI) was obtained:

(VI)

The cyanoethylation of the tertiary acetylene alcohol obtained from mesitylene oxide proceeds readily. The yield of β-cyanoethyl ether (VII) was 73%:

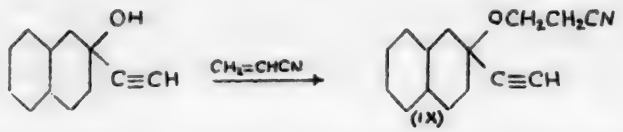
(VII)

1.Ethynylcyclohexanol reacts smoothly with acrylonitrile in a dioxane solution, and forms a 93% yield of the liquid β-cyanoethyl ether (VIII):



(VIII)

The reaction of 2-ethynyldecalol-2 with acrylonitrile in a dioxane solution leads to the formation of an 89% yield of the β-cyanoethyl ether (IX):

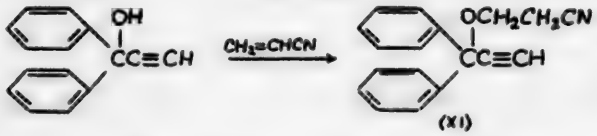


(IX)

In a dioxane solution, the acetylene alcohol from acetophenol reacts readily with acrylonitrile and forms an almost quantitative yield (97%) of the β-cyanoethyl ether (X):

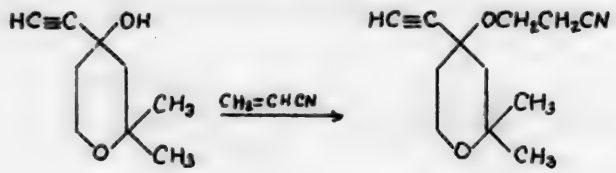
(X)

Diphenylethynylcarbinol also reacts readily and smoothly with acrylonitrile in a dioxane solution, forming an 81% yield of the β-cyanoethyl ether (XI):



(XI)

From the acetylene alcohol (XII), containing a pyran ring, a 77% yield of the corresponding β-cyanoethyl ether (XIII) was obtained:



(XII) (XIII)

EXPERIMENTAL

All the experiments on the cyanoethylation of the acetylene alcohols were carried out in a three-necked flask equipped with a mechanical stirrer, thermometer and reflux condenser. To the mixture of the acetylene alcohol and the catalyst, acrylonitrile was added from a dropping funnel through the adapter of the reflux condenser. The acetylene alcohols were obtained by condensation of aldehydes and ketones with acetylene in the presence of powdered potassium hydroxide, under an acetylene pressure of 5-8 atm [2].

Reaction of acrylonitrile with propylethynylcarbinol. To a mixture of 39.2 g (0.4 mole) of propylethynylcarbinol (b.p. 143.5°) and 3 g of a 40% aqueous solution of potassium hydroxide, 21.2 g (0.4 mole) of acrylonitrile was added,

with energetic stirring, at such a rate as not to raise the temperature of the mixture above 25°. After addition of the acrylonitrile the mixture was stirred at room temperature for 4 hours, and then it stood over night. On the next day, the alkali was neutralized with hydrochloric acid (1:1), the potassium chloride which precipitated was filtered off, and the filtrate was vacuum distilled.

We obtained 44.8 g of the β-cyanoethyl ether (I) with a b.p. of 90-91° at 6.5 mm, n_D^{20} 1.4432, d_4^{20} 0.9243, MR_D 43.34, calculated 43.16.

Found %: N 8.94, 9.05. $C_9H_{13}ON$. Calculated %: N 9.27.

3.8 g of the original carbinol in the experiment was recovered.

The cyanoethylation of the remaining acetylene alcohols was carried out in a similar way.

Reaction of acrylonitrile with isopropylethynylcarbinol. In the reaction 49 g (0.5 mole) of isopropylethynylcarbinol (b.p. 133°), 3.5 g of a 40% aqueous solution of potassium hydroxide, and 26.5 g (0.5 mole) of acrylonitrile were taken.

We obtained 37.5 g of the β-cyanoethyl ether (II) with a b.p. of 83-85° at 5.5 mm, n_D^{20} 1.4405, d_4^{20} 0.9266, MR_D 42.98; calculated 43.16.

Found %: N 9.29, 9.45. $C_9H_{13}ON$. Calculated %: N 9.27.

From the experiment 9.4 g of the original carbinol was recovered.

Reaction of acrylonitrile with β-phenylethyethynylcarbinol. In the reaction 25.5 g (0.16 mole) of β-phenylethylethynylcarbinol (III) (b.p. 125-126° at 10 mm), 2 g of a 40% aqueous solution of potassium hydroxide, and 8.5 g (0.16 mole) of acrylonitrile were taken.

We obtained 24.2 g of the β-cyanoethyl ether (IV) with a b.p. of 141-143° at 3 mm, n_D^{20} 1.5135, d_4^{20} 1.0207, MR_D 62.77; calculated 62.65.

Found %: N 6.69, 6.90. $C_{14}H_{15}ON$. Calculated %: N 6.57.

From the experiment 2.9 g of the original carbinol was recovered.

Reaction of acrylonitrile with methylethylethynylcarbinol. In the reaction 88 g (0.9 mole) of methylethylethynylcarbinol (b.p. 121-122°), 6 g of a 40% aqueous solution of potassium hydroxide, and 48 g (0.9 mole) of acrylonitrile were taken.

We obtained 103 g of the β-cyanoethyl ether of methylethylethynylcarbinol (VII) with a b.p. of 67-68° at 3.5 mm, 64° at 2.5 mm, n_D^{20} 1.4401, d_4^{20} 0.9255, MR_D 43.00; calculated 43.16.

Found %: N 9.39, 9.37. $C_9H_{13}ON$. Calculated %: N 9.27.

From the experiment 18.8 g of the original carbinol was recovered.

Reaction of acrylonitrile with dipropylethynylcarbinol. In the reaction 23.5 g (0.17 mole) of dipropylethynylcarbinol (b. p. 173-174°), 2 g of a 40% aqueous solution of potassium hydroxide, and 9.0 g (0.17 mole) of acrylonitrile were taken.

We obtained 17.1 g of the β-cyanoethyl ether of dipropylethynylcarbinol (VIII) with a b.p. of 98-99° at 4 mm, 102-103° at 5 mm, n_D^{20} 1.4482, d_4^{20} 0.9078, MR_D 56.93; calculated 57.01.

Found %: N 7.38, 7.36. $C_{12}H_{19}ON$. Calculated %: N 7.25.

From the experiment 10.5 g of the original carbinol was recovered.

Reaction of acrylonitrile with methylisobutenylethynylcarbinol. In the reaction 20 g (0.161 mole) of methylisobutenylethynylcarbinol (b.p. 61-64° at 17 mm), 2 g of a 40% aqueous solution of potassium hydroxide, and 8.6 g (0.162 mole) of acrylonitrile were taken.

We obtained 18.3 g of the β-cyanoethyl ether (VII) with a b.p. of 98-100° at 5 mm, n_D^{20} 1.4647, d_4^{20} 0.9426, MR_D 51.88; calculated 51.93.

Found %: N 8.36, 8.37. $C_{11}H_{15}ON$. Calculated %: N 7.91.

From the experiment 2.5 g of the original carbinol was recovered.

Reaction of acrylonitrile with 1-ethynylcyclohexanol. In the reaction 62 g (0.5 mole) of 1-ethynylcyclohexanol (b.p. 179°), 4.5 g of a 40% aqueous solution of potassium hydroxide, 50 ml of anhydrous dioxane, and 26.5 g (0.5 mole) of acrylonitrile were taken.

We obtained 67.5 g of the β-cyanoethyl ether of 1-ethynylcyclohexanol (X) with a b.p. of 92-95° at 3 mm, n_D^{20} 1.4745, d_4^{20} 0.9926, MR_D 50.16; calculated 50.19.

Found %: N 7.86, 7.80. $C_{11}H_{15}ON$. Calculated %: N 7.91.

From the experiment 10.9 g of the original carbinol was recovered.

Reaction of acrylonitrile with 2-ethynyldecalol-2. In the reaction 36 g (0.2 mole) of 2-ethynyldecalol-2 (b.p. 100-101° at 4 mm), 50 ml of anhydrous dioxane, 3 g of a 40% aqueous solution of potassium hydroxide, and 11 g (0.2 mole) of acrylonitrile were taken.

We obtained 34.1 g of the β-cyanoethyl ether of 2-ethynyldecalol-2 (IX) with a b.p. of 150-153° at 4.5 mm, n_D^{20} 1.4976, d_4^{20} 1.0880, MR_D 66.06; calculated 66.47.

Found %: N 6.34, 6.52. $C_{15}H_{21}ON$. Calculated %: N 6.06.

From the experiment 6.5 g of the original carbinol was recovered.

Reaction of acrylonitrile with methylphenylethynylcarbinol. In the reaction 72 g (0.5 mole) of methylphenylethynylcarbinol (b.p. 106-107° at 15 mm), 60 ml of anhydrous dioxane, 7 g of a 40% aqueous solution of potassium hydroxide, and 26.5 g (0.5 mole) of acrylonitrile were taken.

We obtained 73.7 g of the β-cyanoethyl ether of methylphenylethynylcarbinol (X) with a b.p. of 115-118° at 3.5 mm, n_D^{20} 1.5124, d_4^{20} 1.0356, MR_D 57.70; calculated 58.03.

Found %: N 7.32, 7.26. $C_{13}H_{13}ON$. Calculated 7.04.

From the experiment 16.5 g of the original carbinol was recovered.

Reaction of acrylonitrile with diphenylethynylcarbinol. In the reaction 55 g (0.264 mole) of diphenylethynylcarbinol (b.p. 125-126° at 1 mm), 100 ml of anhydrous dioxane, 4.5 g of a 40% aqueous solution of potassium hydroxide, and 14.5 g (0.274 mole) of acrylonitrile were taken.

We obtained 54.3 g of the β-cyanoethyl ether of diphenylethynylcarbinol (XI) with a b.p. of 167-175° at 3.5 mm; m.p. 84-85° (from a mixture of petroleum ether and acetone).

Found %: N 5.68, 5.43. $C_{18}H_{15}ON$. Calculated %: N 5.36.

From the experiment 1.9 g of the original carbinol was recovered.

Reaction of acrylonitrile with 2,2-dimethyl-4-ethynyltetrahydro-4-pyranol. In the reaction 85 g (0.552 mole) of 2,2-dimethyl-4-ethynyltetrahydro-4-pyranol (XII) (b.p. 87-89° at 3 mm), 150 ml of anhydrous dioxane, 6 g of a 40% aqueous solution of potassium hydroxide, and 29.5 g (0.555 mole) of acrylonitrile were taken.

We obtained 85.8 g of the β-cyanoethyl ether (XIII) with a b.p. of 122-125° at 3 mm; n_D^{20} 1.4719, d_4^{20} 1.0984, MR_D 56.04; calculated 56.46.

Found %: N 7.32, 7.17. $C_{12}H_{17}O_2N$. Calculated %: N 6.76.

From the experiment 2.1 g of the original carbinol was recovered.

SUMMARY

1. For the first time, the cyanoethylation of a series of secondary and tertiary acetylene alcohols with different substituents was carried out, and in this way we obtained high yields of the β-cyanoethyl ethers of propylethynylcarbinol, isopropylethynylcarbinol, β-phenylethylethynylcarbinol, methylethylethynylcarbinol, dipropylethynylcarbinol, 1-ethynylcyclohexanol, 2-ethynyldecalol-2, methylisobutene-(1)-ethynylcarbinol, methylphenylethynylcarbinol, diphenylethynylcarbinol and 2,2-dimethyl-4-ethynyltetrahydro-4-pyranol.

2. It was shown that under comparable reaction conditions the size and degree of branching of the radicals in the acetylene alcohols did not have a substantial effect on the yield of the corresponding β-cyanoethyl ethers.

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[1] I. N. Nazarov, G. A. Shvekgeimer, J. Gen. Chem., 24, 157 (1954).*

[2] I. N. Nazarov, I. L. Kotlyarevsky, V. F. Ryabchenko, J. Gen. Chem., 23, 1900 (1953).**

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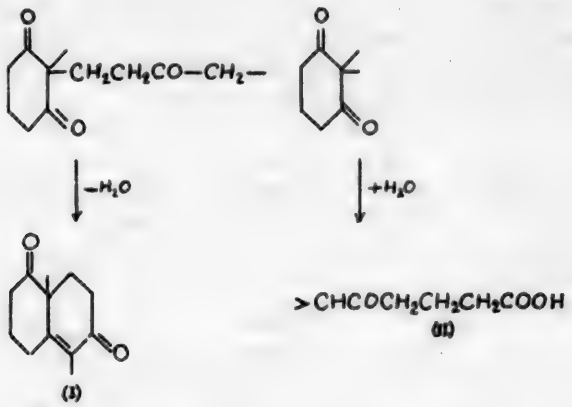
* See Consultants Bureau Translation, page 157.

** See Consultants Bureau Translation, page 2011.

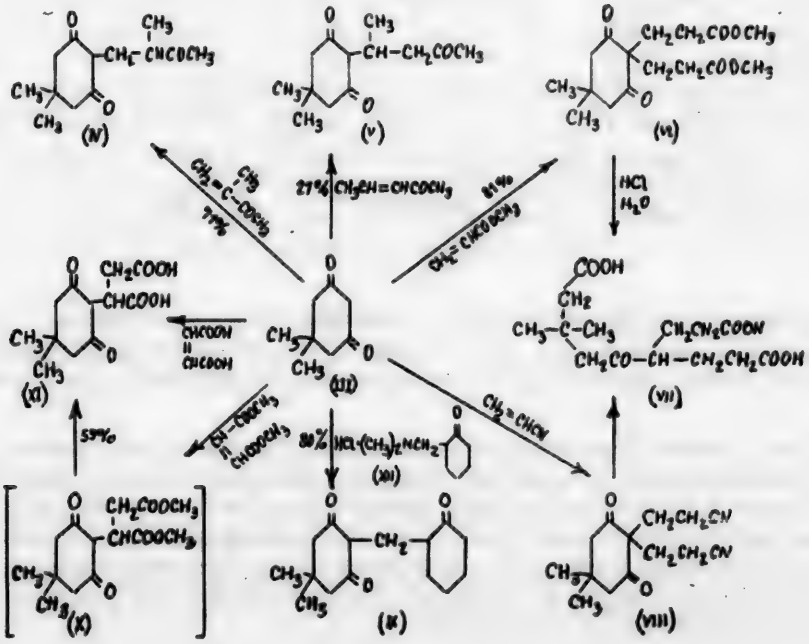
CYCLIC β-DIKETONES IN ADDITION REACTIONS

I. N. Nazarov and S. I. Zavyalov

We showed earlier [1-3] that dihydroresorcinol and its derivatives condense with vinyl ketones and acrylonitrile, forming compounds which are not readily available by other methods, and which may be used in the synthesis of steroids and related substances [4]. In order to follow the effect of the ring on the reactivity of the β-diketonic group, it was of interest to investigate more extensively the behavior of the cyclic β-diketones in addition reactions. Moreover, an exploration of the methods of introduction of the dihydroresorcinol ring into the molecule of organic compounds also was of preparative interest, since in the presence of this ring the compounds can easily be converted to the higher aliphatic keto acids (II) and the dicyclic diketones of type (I).

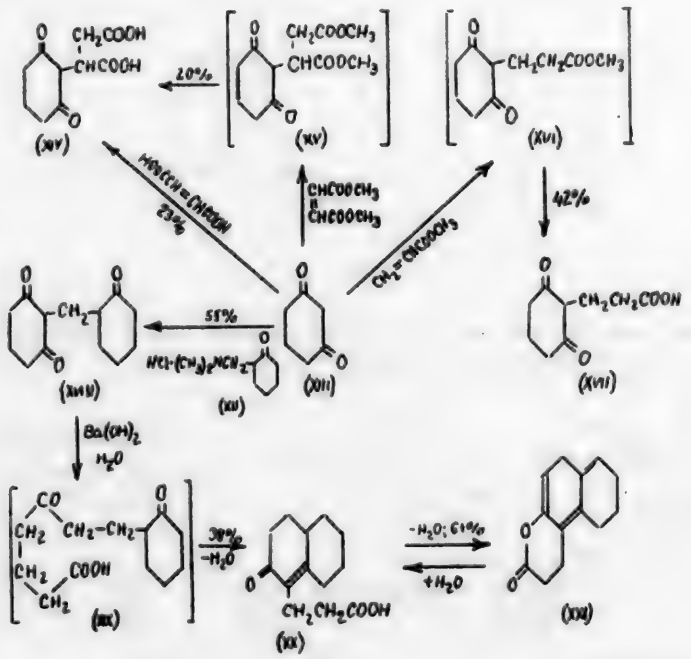


In the present work it was found that the cyclic β-diketones, which have no substituents between the carbonyl groups, react with the α- and β-substituted α,β-unsaturated ketones.



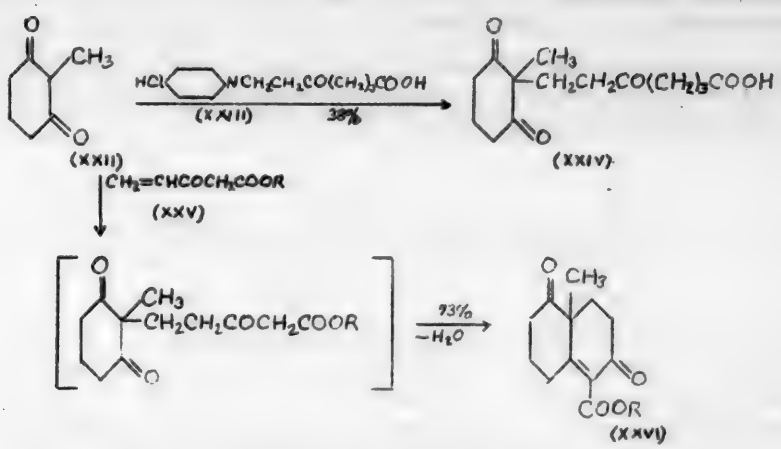
Thus, on boiling a water-dioxane solution of the Na-derivative of dimedon (III) with methyl isopropenyl ketone and ethylidene acetone, the corresponding triketones (IV) and (V) were formed. Conduction of the reaction in a medium of aqueous dioxane gave the best results. For example, the condensation of methyldihydroresorcinol (XXII) with carbethoxymethyl vinyl ketone (XXV) in a methanol solution gave a yield of only 57%, whereas in aqueous dioxane the yield for this reaction amounts to 73% and at the same time we can separate the keto form of 1,6-diketo-5-carbethoxy-9-methyl-$\Delta^{5(10)}$-octalin (XXVI) in the pure crystalline form. The heating of Na-dimedon with an excess of acrylonitrile in a tert-butyl alcohol at 80° for 6 hours leads to the formation of an 80% yield of the monocyanethyl derivative, whereas in an aqueous dioxane solution under the same conditions a 63% yield of the bis-addition product (VIII) forms. Thus, the polarity of the solvent favorably influences the course of the Michael reaction of the cyclic β-diketones.

We may successfully use the β-aminoketone hydrochlorides, which are easily obtained by the Mannich reaction, as a source of the α,β-unsaturated ketones. For example, on reaction of 2-dimethylaminomethylcyclohexanone hydrochloride (XII) with dimedon (III) or dihydroresorcinol (XIII), the dicyclic triketones (IX) and (XVIII) are obtained in high yields. In these condensations it is possible to use much less than the equivalent quantity of alkali, since dialkylamine, which also binds hydrogen chloride, is separated in proportion to the entry of β-aminoketone into reaction. Hydrolysis of the triketone (XVIII) by baryta water leads to the formation of the unsaturated dicyclic keto acid (XX), which arises from the hydrolytic cleavage of the dihydroresorcinol ring, with subsequent cyclization of the diketone (XIX). It was found that the dimedon ring of the triketone (IX) is extremely stable toward hydrolysis: the initial product was recovered almost completely from the reaction mixture, even after a 30-hour boiling with baryta water. On boiling with acetic anhydride in the presence of traces of sodium acetate, the keto acid (XX) cyclized to the lactone (XXI), which was easily converted to the original keto acid (XX) by treatment with alkali.



β-Aminoketones, which contain a free carboxyl group, can react with the cyclic β-diketones, since the reaction is carried out in homogeneous aqueous solutions. Thus, the condensation of methyldihydroresorcinol (XXII) with γ-(β'-piperidinopropionyl)-butyric acid hydrochloride (XXIII), in the presence of an equivalent of alkali, gives the triketo acid (XXIV).

Acrylic ester, like acrylonitrile, condenses readily with the cyclic β-diketones at 100°, forming the corresponding addition products. Upon reaction of dimedon (III) with an excess of acrylic ester in a water-dioxane medium, in the presence of a small quantity of alkali or soda, an almost quantitative yield of the bis-addition product (VI) formed, the structure of which was confirmed by its saponification to the previously described keto tricarboxylic acid (VII), which was obtained from di-(β-cyanoethyl)-dimedon (VIII). By the use of equimolecular quantities of reagents and alkali, dihydroresorcinol (XIII) and acrylic ester gave diketocarboxylic acid (XVII), which was formed as a result of the saponification of the ester (XVI) during the process of condensation.



The introduction of substituents at the double bond of acrylic ester and acrylonitrile leads to a sharp decrease of the reactivity in a number of these compounds. Methacrylic ester, methacrylonitrile and crotonic ester, on heating for 8-10 hours at 100°, did not add to dihydroresorcinol (XIII), dimedon (III) and methyldihydroresorcinol (XXII). Maleic ester constitutes an exception, which under the influence of alkali does condense with dimedon (III) and dihydroresorcinol (XIII); thus, the dicarboxylic acids (XI) and (XIV), instead of the expected corresponding diesters (X) and (XV) formed, since the diesters undergo saponification during the same reaction.

α,β-Unsaturated carboxylic acids (acrylic acid, crotonic acid, fumaric acid) do not react with the cyclic β-diketones even on prolonged heating of the reagents in aqueous solutions. Moreover, maleic acid readily condenses at 100°, in the presence of 3 equivalents of alkali, forming the previously mentioned derivatives of succinic acid, (XI) and (XIV), obtained from maleic ester. Thus, according to the extent of the decrease of activation of the double bond of the α,β-unsaturated compounds in reactions with the cyclic β-diketones, the polar groups can be arranged in the following series: CO, CN, COOR, COOH.

The above-stated experimental data enable us to conclude that dihydroresorcinol derivatives, in spite of the high proton mobility of the hydrogen atom, exhibit a relatively weak capacity for the Michael reaction. The distinctly expressed acid properties of these compounds cannot of themselves be the source of this phenomenon, since the use of equivalent quantities of alkali catalyst does not lead to any significant increase of the reactivity. Thus, for example, at room temperature the Na-derivative of dimedon, even over a period of two days, does not react with acrylonitrile.

Spectroscopic investigations [5] and bromometric titration data [6, 7], which indicate the complete enolization of dimedon and dihydroresorcinol in aqueous solutions, offer a basis for assuming that, precisely in this property of the cyclic β-diketones lies the reason for their low capacity for the Michael condensation, since stabilization of the enol cannot serve as a hindrance to the accomplishment of this reaction in which the keto form should participate. This assumption is confirmed completely by the chemical properties of readily enolizing ketones of different structures.

α-Acetylacetoacetic ester (XXVII), which is 100% enolized in aqueous solution, in spite of the high mobility of hydrogen, does not undergo cyanoethylation at 70° in the presence of $\frac{1}{5}$ equivalent of sodium tert-butyl. Under more severe conditions, the cleavage of α-acetylacetoacetic ester of acetoacetic ester occurs, and the latter also undergoes cyanoethylation in the usual way with the formation of the dinitrile (XXVIII).

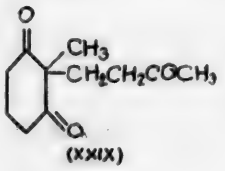
(XXVII) (XXVIII)

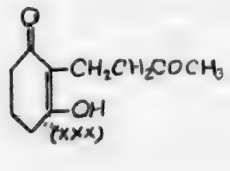
According to the data of I. N. Nazarov and L. N. Terekhova [8], and also of Henecka [9], the decrease of the capacity of malonic ester, acetoacetic ester and acetylacetone for the Michael reaction proceeds directly, i.e., it is parallel to the increase of the capacity of these compounds for enolization. For the same reason, the aliphatic and aliphatic-aromatic β-diketones undergo cyanoethylation more difficultly than do the β-keto esters [10].

At the present time it can be considered as demonstrated that the CO-group activates the hydrogen atom more strongly than does the COOR-group [11, 12]. However, an accumulation of activating groups leads to an increase of

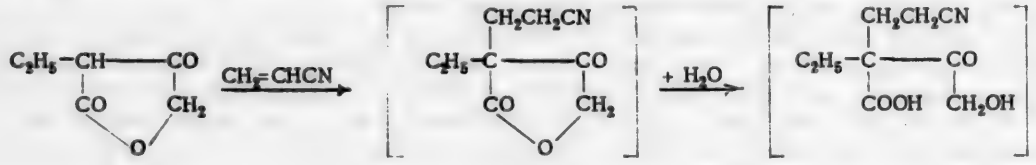
enolization of the ketones and, consequently, to a weakening of the capacity of the latter for the Michael reaction, in spite of the increase of the mobility of the hydrogen atoms.

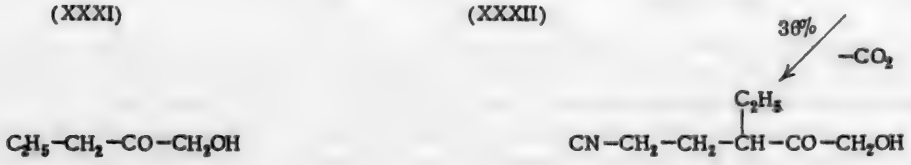
The retarding action of enolization was recorded also for other reactions; 2-methyl-2-(γ-ketobutyl)-dihydroresorcinol (XXIX) much more readily undergoes hydrolytic cleavage and cyclization than does 2-(γ-ketobutyl)-dihydroresorcinol (XXX) [2], since the latter is a highly enolized compound.


(XXIX)


(XXX)

Although the enolization of a ketone also hampers the course of a reaction with participation of the keto form, nevertheless, it does not appear to be an insupperable obstacle for the Michael condensation; the highly enolized α-alkyltetronic acid, the data of Henecka [9] notwithstanding, reacts with methyl vinyl ketone [1] and acrylonitrile at elevated temperatures. On cyanoethylation of pentynic acid (XXXI) we obtained the ketol (XXXIII), the formation of which can be accounted for only by the hydrolytic cleavage and decarboxylation of the condensation product (XXXII). The possibility of cleavage of the same pentynic acid, and subsequent cyanoethylation of the ketol (XXXIV), is entirely excluded since pentynic acid is stable toward the action of an aqueous solution of alkali.


(XXXI) (XXXII)


(XXXIV) (XXXIII)

EXPERIMENTAL

Condensation of Dimedon with Methyl Isopropenyl Ketone

A solution of 0.3 g of potassium hydroxide in 8 ml of water, 0.7 g of dimedon (III) (b.p. 144-145°) and 1 g of methyl isopropenyl ketone (b.p. 98-100°, n_D^{20} 1.4238) in 5 ml of dioxane was boiled under reflux for 5 hours. After extraction of the reaction product with chloroform we obtained 0.8 g (71%) of 2-(β-methyl-γ-ketobutyl)-dimedon (IV) with a m.p. of 119-120° (from aqueous dioxane). The substance was dissolved in an aqueous soda solution.

Found %: C 69.01, 68.95; H 8.72, 8.81. $C_{13}H_{20}O_3$. Calculated %: C 69.30; H 8.90.

Condensation of Dimedon with Ethylidene Acetone

The reaction was carried out as described above. From 0.7 g of dimedon and 1 g of ethylidene acetone (b.p. 121-123°, n_D^{20} 1.4390) we obtained 0.3 g (27%) of 2-(α-methyl-γ-ketobutyl)-dimedon (V) with a m.p. of 73-74° (from aqueous acetone).

Found %: C 69.35, 69.51; H 9.02, 9.23. $C_{13}H_{20}O_3$. Calculated %: C 69.3; H 8.90.

Reaction of Methyldihydroresorcinol with Carbethoxy Methyl Vinyl Ketone

4 g of methyldihydroresorcinol (b.p. 208-209°) (XXII) was added to a solution of 0.03 g of sodium hydroxide in 8 ml of water, and then 4.5 g of carbethoxy methyl vinyl ketone (XXV) (b.p. 76-78° at 18 mm, n_D^{20} 1.4585 [2]) in 8 ml of dioxane was introduced. The mixture was heated at 85-95° for 3 hours, and on cooling was extracted with ether. The precipitate of methyldihydroresorcinol (0.7 g) which separated was filtered off, and after evaporation of the ether

solution the residue was vacuum distilled. We obtained 4.4 g (73%) of 1,6-diketo-5-carbethoxy-9-methyl-$\Delta^{5(10)}$-octalin (XXVI) with a b.p. of 174-177° at 0.5 mm.

Found%: C 67.75, 67.70; H 7.39, 7.26. $C_{14}H_{18}O_4$. Calculated %: C 67.20; H 7.20.

The substance gave a dark-violet coloration with ferric chloride. On standing the keto form (2.3 g) with a m.p. of 65-66° (from a mixture of ether and n-hexane) separated, but it gave no coloration with ferric chloride

Found%: C 67.05, 67.26; H 7.11, 7.09. $C_{14}H_{18}O_4$. Calculated %: C 67.2; H 7.2.

Upon hydrogenation over a Pt-catalyst in methanol, the crystalline and liquid forms of the substance (XXVI) were converted to the previously described 1,6-diketo-9-methyl-5-carbethoxydecalin [2].

Cyanoethylation of Dimedon

1) 0.35 g of dimedon was treated with a solution of 0.03 g of potassium hydroxide in 2 ml of water, and after driving off the water in vacuo, the residue was mixed with 5 ml of tert-butyl alcohol. The resulting solution was heated with 2 g of acrylonitrile at 80° for 6 hours. We obtained 0.38 g (80%) of (β-cyanethyl)-dimedon with a m.p. of 151-152° (from water) [3].

2) 0.35 g of dimedon and 2 g of acrylonitrile in 3 ml of dioxane were added to a solution of 0.03 g of potassium hydroxide in 2 ml of water. The mixture was heated at 80° for 6 hours. We obtained 0.35 g (63%) of di-(β-cyanoethyl)-dimedon with a m.p. of 146-147° (from aqueous methanol) [3].

Reaction of Dimedon with 2-Dimethylaminomethylcyclohexanone Hydrochloride

A mixture of 0.3 g of potassium hydroxide in 10 ml of water, 0.7 g of dimedon and 1 g of 2-dimethylaminomethylhexanone hydrochloride (m.p. 149-150°) [13], was heated at 90-95° for 30 minutes. The solution was acidified to Congo with dilute (1:1) hydrochloric acid, and the reaction product which separated was filtered off. We obtained 1 g (80%) of the dicyclic triketone (IX) with a m.p. of 182-183° (from aqueous dioxane).

Found%: C 71.92, 71.93; H 8.82, 8.85. $C_{19}H_{22}O_3$. Calculated %: C 72.0; H 8.8.

Reaction of Dihydroresorcinol with 2-Dimethylaminomethylcyclohexanone Hydrochloride

A mixture of 0.2 g of potassium hydroxide in 30 ml of water, 13 g of dihydroresorcinol (XIII), and 18 g of 2-dimethylaminomethylcyclohexanone hydrochloride was boiled under reflux for 1 hour, and after the previously mentioned treatment we separated 16 g (55%) of the triketone (XVIII), with a m.p. of 164-165° (from aqueous dioxane).

Found%: C 70.48, 70.39; H 8.26, 8.43. $C_{13}H_{18}O_3$. Calculated %: C 70.3; H 8.2

Hydrolytic cleavage of the triketone (XVIII). 80 g of barium hydroxide in 250 ml of water and 16 g of the triketone (XVIII) were boiled under reflux for 30 hours. On cooling, the mixture was acidified (to Congo) with concentrated hydrochloric acid. The precipitate which separated was filtered off and washed with ether. We obtained 6 g (38%) of the keto acid (XX), with a m.p. of 103-104° (from aqueous acetone).

Found%: C 70.37, 70.30; H 8.36, 8.38; $C_{13}H_{18}O_3$. Calculated %: C 70.3; H 8.2.

Found: titration equiv. 219. $C_{13}H_{18}O_3$. Calculated: titration equiv. 222.

Lactonization of the keto acid (XX). A mixture of 6 g of the keto acid (XX), 30 ml of acetic anhydride and 0.01 g of anhydrous sodium acetate was boiled under reflux for 5 hours. After removal of the volatile products in vacuo, the residue was distilled. We obtained 3.4 g (61%) of the lactone (XXI) with a b.p. of 145-147° at 0.5 mm, n_D^{20} 1.5660.

Found%: C 76.61, 76.80; H 7.79, 7.64. $C_{13}H_{16}O_2$. Calculated %: C 76.4; H 7.8.

The lactone (XXI) was converted to the original keto acid (XX) by heating it with dilute alkali.

Reaction of Methyldihydroresorcinol with γ-(β'-piperidinopropionyl)-butyric Acid Hydrochloride

A mixture of 0.3 g of potassium hydroxide in 10 ml of water, 0.6 g of methyldihydroresorcinol (XXII), and 1.3 g of γ-(β'-piperidinopropionyl)-butyric acid hydrochloride (XXIII) (m.p. 158-159°) [14] was boiled under reflux for 3 hours. The resulting solution was acidified (to Congo) with dilute (1:1) hydrochloric acid and extracted with chloroform. After removal of the solvent, the residue gradually crystallized. We obtained 0.5 g (38%) of the triketo acid (XXIV) with a m.p. of 143-144° (from water).

Found%: C 62.93, 62.95; H 7.73, 7.48. $C_{14}H_{20}O_5$. Calculated %: 62.7; H 7.5.

Found: titration equiv. 265. $C_{14}H_{20}O_5$. Calculated: titration equiv. 268.

Condensation of Dimedon with Acrylic Ester

To a solution of 0.05 g of sodium hydroxide in 5 ml of water we added 1 g of dimedon, and then 3 g of the methyl ester of acrylic acid in 6 ml of dioxane. The mixture was boiled under reflux for 7 hours; on cooling, it was concentrated in vacuo to $\frac{1}{3}$ of its original volume, and the crystalline product which separated was filtered off. We obtained 1.8 g (81%) of 2,2-di-(β-carbomethoxyethyl)-dimedon (VI) with a m.p. of 80-81° (from a mixture of ether and petroleum ether). The substance did not dissolve in an aqueous solution of soda.

Found %: C 61.93, 62.06; H 7.89, 8.01. $C_{16}H_{24}O_6$. Calculated %: C 61.6; H 7.7.

Saponification of 2,2-di-(β-carbomethoxyethyl)-dimedon (VI). 1.3 g of the substance (VI) and 30 ml of dilute (1:1) hydrochloric acid were boiled under reflux for 6 hours. On cooling, the solution was evaporated to dryness in vacuo. The residue crystallized almost completely on standing. We obtained 1 g (67%) of the tricarboxylic acid (VII), with a m.p. of 109-110° (from a mixture of benzene and dioxane), which gave no m.p. depression with the 2,2-dimethyl-4-keto-5-(2'-carboxyethyl)-heptane-1,7-dicarboxylic acid obtained from 2,2-di-(β-cyanoethyl)-dimedon (VIII) [3].

Condensation of Dihydroresorcinol with Acrylic Ester

To a solution of 1.1 g of potassium hydroxide in 5 ml of water we added 2.2 g of dihydroresorcinol, then introduced 2 g of the methyl ester of acrylic acid, and the mixture was boiled under reflux for 3 hours. The solution was filtered and concentrated in vacuo to $\frac{1}{3}$ of the original volume. Upon acidification with dilute (1:1) hydrochloric acid we separated 1.5 g (42%) of the triketo acid (XVII) with a m.p. of 188-189° (from water).

Found %: C 58.81, 58.70; H 6.55, 6.46. $C_9H_{12}O_4$. Calculated %: C 58.7; H 6.5.

Reaction of Dimedon with Maleic Ester

To a solution of 0.15 g of sodium hydroxide in 10 ml of water we added 0.5 g of dimedon and then introduced 0.6 g of the methyl ester of maleic acid in 8 ml of dioxane. The mixture was boiled under reflux for 3 hours, and on cooling was extracted with ether. The aqueous solution was acidified to Congo with dilute (1:1) hydrochloric acid, and evaporated in vacuo. In this way, we separated 0.5 g (55%) of the diketo diacid (XI) with a m.p. of 219-220° (from water).

Found %: C 56.01, 56.30; H 6.21, 6.05. $C_{12}H_{16}O_6$. Calculated %: C 56.2; H 6.3.

Reaction of Dihydroresorcinol with Maleic Ester

The reaction was carried out as indicated above. From 1.1 g of dihydroresorcinol and 4 g of maleic ester we obtained 0.43 g (20%) of the diketo diacid (XIV) with a m.p. of 192-193° (decomposed) (from water).

Found %: C 52.51, 52.50; H 5.37, 5.34. $C_{10}H_{12}O_6$. Calculated %: C 52.6; H 5.3.

Condensation of Dihydroresorcinol with Maleic Acid

A mixture of 1.7 g of potassium hydroxide in 10 ml of water, 1.1 g of dihydroresorcinol, and 1.1 g of maleic acid was boiled under reflux for 7 hours. After acidification to Congo with dilute (1:1) hydrochloric acid, the solution was evaporated in vacuo. Thus, we precipitated 0.5 g (23%) of the previously mentioned diketo diacid (XIV) with a m.p. of 192-193°.

Condensation of Dimedon with Maleic Acid

The reaction was carried out as indicated above. From 0.35 g of dimedon and 0.3 g of maleic acid, we obtained 0.5 g (78%) of the previously mentioned diketo diacid (XI), with a m.p. of 219-220°.

Attempts to Cyanoethylate α-Acetylacetoacetic Ester

1) To a solution of the Na-derivative of α-acetylacetoacetic ester, prepared from 0.05 g of sodium and 3 g of the ester in 10 ml of tert-butyl alcohol, we added 2 g of acrylonitrile; the mixture was heated at 60-70° for 10 hours. After removal of the solvent in vacuo, the residue was neutralized with dilute (1:1) hydrochloric acid and extracted with ether. The main quantity of the product (2.3 g) consisted of unreacted α-acetylacetoacetic ester with a b.p. of 91-92° at 10 mm; n_D^{20} 1.4748; the melting point of its cupric salt was 150-151° [15].

2) To a solution of the K-derivative of α-acetylacetoacetic ester, prepared from 0.3 g of potassium and 3 g of the ester in 10 ml of tert-butyl alcohol, we added 2 g of acrylonitrile; the mixture was heated at 75-80° for 5 hours. After the treatment indicated above, we obtained 1 g of the original α-acetylacetoacetic ester and 0.3 g of α,α-di-(β-cyanoethyl)-acetoacetic ester (XXVIII) with a b.p. of 190-200° at 2 mm and a m.p. of 81-82° [10]. The substance gave no m.p. depresion with a sample obtained by the cyanoethylation of acetoacetic ester.

Cyanoethylation of Pentynic Acid (XXXI)

The Na-salt of pentynic acid, prepared from 1.8 g of pentynic acid (m.p. 125-126°) [16] and 2 g of acrylonitrile in 15 ml of aqueous dioxane (2:1) was boiled under reflux for 4 hours. On cooling, the solution was extracted with chloroform, and after removal of the solvent the residue was vacuum distilled. We obtained 0.8 g (36%) of the ketol (XXXIII) with a b.p. of 130-140° at 0.5 mm and a m.p. of 104-105° (from benzene). The substance instantly reduced copper acetate in the cold.

Found %: C 61.74, 61.71; H 8.33, 8.53; N 9.30, 9.40. $C_{10}H_{13}O_2N$. Calculated %: C 61.9; H 8.4; N 9.0.

SUMMARY

1. It was shown that dihydroresorcinol and dimedon enter into the Michael condensation with α- and β-substituted unsaturated ketones, acrylic ester, maleic ester and maleic acid.

2. According to the extent of the decrease of the double bond activation of the α,β-unsaturated compounds in reactions with cyclic β-diketones, the polar groups may be arranged in the following series: CO, CN, COOR, COOH.

3. It was found that the β-aminoketone hydrochlorides may be used successfully as a source for the production of α,β-unsaturated ketones in reactions with dihydroresorcinol and its derivatives.

4. The cyanoethylation of pentynic acid was carried out, and it showed the inaccuracy of Henecka's assertion that α-alkyltetronic acid does not enter into the Michael reaction.

5. It was found that dihydroresorcinol derivatives enter into the Michael reaction more difficultly than do cyclohexanone, malonic ester and acetoacetic ester, and it was assumed that the cause of this phenomenon lay in the enolization of the cyclic β-diketones.

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* See Consultants Bureau Translation, page 309.

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INVESTIGATIONS IN THE FIELD OF CONJUGATED SYSTEMS

LVII. CONDENSATION OF PROPARGYL ALDEHYDE WITH PIPERYLENE AND ISOPRENE

A. A. Petrov and N. P. Sopov

In the chemical literature in the last 5-10 years much attention has been devoted to the mechanism of the diene synthesis, one of the methods for the elucidation of which is the study of the order of the homocyclization of the asymmetrical dienes. A number of articles by the authors of the present report and also by other investigators have been devoted to the latter problem. However, all this vast material pertains chiefly to reactions of the dienes with the ethylene dienophiles. There is a very small number of works [1-3] on the order of the reaction of the dienes with acetylene dienophiles; therefore, continuing our investigations in the field of the order of the homocyclization of the dienes, we studied the reaction of propargyl aldehyde with two of the simplest asymmetrical dienes – piperylene and isoprene.

The reactions of these hydrocarbons with the ethylene analog of propargyl aldehyde – acrolein – have been studied rather in detail.

The condensation of piperylene with acrolein was first studied by B. A. Arbuzov and coworkers [4], however, the structure of the reaction product was not established by these authors. Later, one of us, by the oxidation of acrolein obtained 2-methyl-Δ^3-tetrahydrobenzoic acid, which formed o-toluic acid on dehydrogenation [5]. Thus, it was found that condensation proceeds here in accordance with the electronic polarization of the components. Such a structure of the condensation product of piperylene and acrolein was further confirmed by B. A. Arbuzov and E. G. Kataev [6] and other investigators [7].

There are also data relative to the structure of the condensation product of acrolein and isoprene. By reaction of isoprene with a Grignard reagent, α-terpineol [8] was obtained, and by distillation over phosphoric anhydride p-xylene was obtained [9].

Both of these syntheses show that the substance obtained has substituents chiefly in the para-position, and consequently, that the reaction proceeds here also in accordance with the electronic polarization of the reagents. However, data relative to the structures of the substances obtained from isoprene were characterized by lower accuracy and enabled us to indicate only the prevailing direction of the homocyclization reaction.

We determined the structure of the condensation products of piperylene and isoprene with propargyl aldehyde by two methods. First, these substances were dehydrogenated to the corresponding aromatic aldehyds by heating over sulfur. Second, by the action of the Grignard reagent, we obtained the corresponding cyclohexadiene alcohols, the dehydration of which yielded aromatic hydrocarbons with radicals in the same positions as in the original aldehydes.

The structure of the hydrocarbons was established by oxidation with nitric acid to the corresponding phthalic acid.

In this way, from piperylene we obtained o-tolualdehyde, which was identified by its constants and by the melting point of its 2,4-dinitrophenylhydrazone, and also by the formation of o-toluic acid by its oxidation.

On the other hand, from the same condensation product we obtained an alcohol, which on dehydration yielded o-methylethylbenzene. o-Phthalic acid was obtained by oxidation of o-methylethylbenzene.

Under similar conditions, the condensation product of propargyl aldehyde with isoprene yielded p-tolualdehyde, p-toluic acid, p-methylethylbenzene, and terephthalic acid, the methyl ester of which melted at 140°.

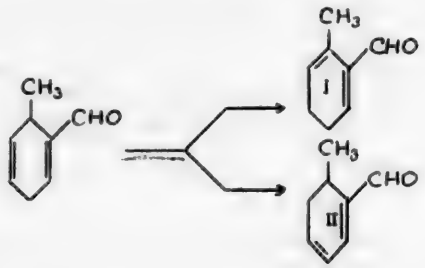
However, it is necessary to point out that in this case the p-nitrophenyl- and 2,4-dinitrophenylhydrazone of the aromatic aldehyde melted somewhat lower than was indicated in the literature for p-tolualdehyde. Possibly this indicates the presence of a small admixture of the meta-isomer.

Thus, the present investigation showed that piperylene and isoprene react with propargyl aldehyde, just as they do with acrolein, in accordance with the electronic polarization of their molecules, which indicates the polar mechanism of this reaction.

In the study of the reaction of piperylene with propargyl aldehyde we encountered the same circumstance which we observed in the condensation of butynone with piperylene [1]: in some cases we obtained a product which differed

sharply in its properties from the usual product of this reaction. The anomalous product had a much higher index of refraction, a much exaggerated molecular refraction, it was observed to be entirely combined on heating with maleic anhydride, and on heating with sulfur it gave, not the aromatic aldehyde, but a resin. All these data enabled us to assume the presence of a conjugated system of double bonds in the anomalous product. Obviously, during the reaction a transference of one of the double bonds occurs. The isomerization of the 1,4-cyclohexadiene aldehydes to the 1,3-cyclohexadiene aldehydes was described in the literature [2]. Isomerization occurs in the presence of acids. It is possible that in those cases when we obtained an anomalous product, traces of acids infiltrated the reaction zone, since this happened just in those experiments in which we used piperylene which was obtained by the dehydration of methylpropenylcarbinol with small amounts of hydrobromic acid.

The isomerization could proceed here in two directions. However, we would more likely expect the formation of product I, since the mobility of the secondary atom is undoubtedly greater than that of the primary atom.



Methyldihydrobenzaldehyde is a liquid with a bitter-almond odor. The ortho-isomer has a more disagreeable odor, which is suggestive of that of hydrocyanic acid. In Table 1 are cited the constants of all the dihydrobenzaldehydes described in the present work and in previous reports [10].

It is obvious from the data of Table 1 that the position of the methyl group in the ring strongly affects the boiling point, the specific gravity and the index of refraction of the aldehydes. For a given value of the molecular refraction, the ortho-derivative has a much lower index of refraction.

The constants of the three 1,4-cyclohexadiene alcohols are cited in Table 2. From the data of Table 2 it is evident that, as in the case of the aldehydes, the position of the methyl group strongly affects the boiling point here, whereas this factor has almost no effect on the other constants.

EXPERIMENTAL

1. Condensation of Piperylene with Propargyl Aldehyde

By heating 6.2 g of the aldehyde and 15 g of piperylene (technical, piperylene content 91%) in 30 ml of toluene for 5 hours at 110°, we obtained 10 g of 2-methyl-$\Delta^{3,6}$-dihydrobenzaldehyde. The yield, based on propargyl aldehyde, was 71%.

45.07 mg sub.: 130.20 mg CO_2; 31.94 mg H_2O. Found %: C 78.84; H 7.93. $C_8H_{10}O$. Calculated %: C 78.65; H 8.25.

The semicarbazone was obtained in an aqueous medium by the usual method. It consisted of colorless flakes (from alcohol).

5.78 mg sub: 1.200 ml N_2 (30°, 760 mm). Found %: N 23.44. $C_9H_{13}ON_3$. Calculated %: N 23.45.

The p-nitrophenylhydrazone consisted of fine yellow needles (from alcohol).

7.24 mg sub: 1.02 ml N_2 (26°, 760 mm). Found %: N 16.07. $C_{14}H_{15}O_2N_3$. Calculated %: N 16.38.

The 2,4-dinitrophenylhydrazone consisted of orange flakes (from a mixture of alcohol and benzene).

6.93 mg sub: 1.10 ml N_2 (26°, 760 mm). Found %: N 18.06. $C_{14}H_{14}O_4N_4$. Calculated %: N 18.53.

3 g of 2-methyldihydrobenzaldehyde was heated for 40 minutes with a small amount of sulfur. The liberation of hydrogen sulfide was observed. The resulting o-tolualdehyde was vacuum distilled. Yield was 1.5 g (50%).

TABLE 1

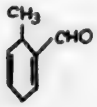
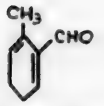
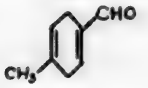
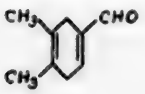
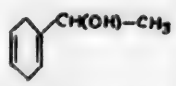
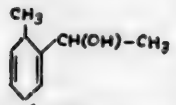
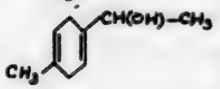
Substance	B.p. (20 mm)	d_4^{20}	n_D^{20}	MR found	MR calc'd.	M.p. of semicarbazones	M.p. of p-nitrophenylhydrazones	M.p. of 2,4-dinitrophenylhydrazones
	80°	1.0230	1.5182	32.04	31.40	204-205°	197-198°	226°
	82-82.5	0.9819	1.5048	36.89	36.02	197	183-185	169-170
	81-83	0.9850	1.5250	38.00	36.02	194	–	165
	95.5-96	0.9943	1.5124	36.88	36.02	202-203	192-193	214-215
	112-113	–	1.5176	–	–	230	218-219	233-234

TABLE 2

Substance	Boiling point (20 mm)	d_4^{20}	n_D^{20}	MR found	MR calculated
	103.5°	0.9943	1.5068	37.15	37.53
	104.5	0.9695	1.5002	41.94	42.15
	115.5-116.5	0.9688	11.5008	42.01	42.15

B.p. 196-198°, d_4^{20} 1.0328, n_D^{20} 1.5462.

The 2,4-dinitrophenylhydrazone had a m.p. of 193-194°.

Literature data [11]: b.p. 197°, d_4^{19} 1.0386, n_D^{19} 1.5490; the 2,4-dinitrophenylhydrazone, m.p. 193-194°.

On oxidation of the aldehyde by heating in a sealed tube with 25% nitric acid on a water bath, we obtained o-toluic acid with a m.p. of 104° (from water). The same melting point was indicated in the literature.

2-Methyldihydrobenzaldehyde (4 g) was cautiously added to a solution of the Grignard reagent obtained from 1.2 g of magnesium. After heating on the water bath for 1 hour, the mixture was poured over ice mixed with a saturated solution of NH_4Cl. After drying over Na_2SO_4, the ether was driven off at ordinary pressure on the water bath, and the reaction products were vacuum distilled; thus, we obtained 3.9 g (87%) of the corresponding alcohol. The constants are given in Table 2.

11.13 mg sub.: 31.78 mg CO_2; 10.40 mg H_2O. 11.00 mg sub.: 31.60 mg CO_2; 10.42 mg H_2O. Found %: C 78.07, 78.40; H 10.40, 10.60. $C_9H_{14}O$. Calculated %: C 78.23; H 10.21.

3 g of the alcohol was distilled with a 10% solution of oxalic acid. The resulting hydrocarbon was dried over $CaCl_2$ and distilled over sodium. 2 g (78%) of the substance was obtained.

B.p. 162-168°, d_4^{20} 0.8792, n_D^{20} 1.5000.

After treatment with a solution of bromine in acetic acid until decolorization ceased, the steam-distilled o-methylethylbenzene had a b.p. of 163-165°, d_4^{20} 0.8805, n_D^{20} 1.5026. Judging from the quantity of bromine consumed, the content of the unsaturated hydrocarbon did not exceed 15%.

Literature data for o-methylethylbenzene [12]: b.p. 165.15°, d_4^{20} 0.8807, n_D^{20} 1.5046.

The aromatic hydrocarbon was oxidized by heating it with 25% nitric acid in a sealed tube at 150-160°. The resulting o-phthalic acid, after recrystallization from water, melted with dehydration at about 184°. The substance dissolved completely and well in hot water, which indicated the absence of any considerable admixture of the difficultly-soluble isophthalic acid.

A sample of the acid obtained was heated with a small quantity of resorcinol and a drop of H_2SO_4. Fluorescein was obtained.

In another experiment, from 12 g of piperylene obtained by the dehydration of methylpropenylcarbinol with hydrobromic acid, and 6.5 g of propargyl aldehyde, we obtained 8 g (52%) of methyldihydrobenzaldehyde and 5.5 g of high-boiling products and resins.

The constants of this sample are given in Table 1.

30.40 mg sub: 87.50 mg CO_2; 21.70 mg H_2O. Found %: C 78.55; H 7.99. $C_9H_{10}O$. Calculated %: C 78.65; H 8.25.

2 g of the substance was heated with 2 g of maleic anhydride on the water bath for 3 hours. We did not succeed in steam-distilling the original aldehyde from the reaction mixture. The condensation product was not carefully studied.

3 g of the aldehyde was heated with sulfur for 30 minutes. We obtained a brown resin, from which we were unable to separate tolualdehyde either by vacuum- or by steam-distillation.

2. Condensation of Isoprene with Propargyl Aldehyde

From 7.5 g of the aldehyde and 11.5 g of isoprene we obtained 12.8 g (76.6%) of 4-methyl-$\Delta^{1,4}$-dihydrobenzaldehyde and 1 g of resin.

38.70 mg sub.: 111.45 mg CO_2; 27.50 mg H_2O. Found %: C 78.59; H 7.95. $C_9H_{10}O$. Calculated %: C 78.65; H 8.25.

The semicarbazone consisted of colorless, fine crystals (from alcohol).

3.49 mg sub: 0.720 ml N_2 (24°, 760 mm). Found %: N 23.71. $C_9H_{13}ON_3$. Calculated %: N 23.45.

The p-nitrophenylhydrazone consisted of orange plates with truncated edges (from alcohol).

4.97 mg sub: 0.730 ml N_2 (27°, 759 mm). Found %: N 16.69. $C_{15}H_{15}O_2N_3$. Calculated %: N 16.38.

The 2,4-dinitrophenylhydrazone consisted of dark-orange needles (from benzene).

4.61 mg sub: 0.749 ml N_2 (27.5°, 762.5 mm). Found %: N 18.51. $C_{15}H_{14}O_4N_4$. Calculated %: N 18.53.

3 g of 4-methyldihydrobenzaldehyde was heated with a small amount of sulfur for 45 minutes. The liberation of hydrogen sulfide was observed. The p-tolualdehyde was vacuum distilled, and then distilled again at ordinary pressure. The yield was 1.5 g (50%).

B.p. 204-205°, d_4^{20} 1.0190, n_D^{20} 1.5453.

The p-nitrophenylhydrazone consisted of orange needle-shaped nodules (from alcohol). The m.p. was 194-195°. The 2,4-dinitrophenylhydrazone consisted of orange-red needles (from benzene). The m.p. was 228-230°.

After several days in contact with the air, the aldehyde was converted to p-toluic acid with a m.p. of 178-180°. The same acid was obtained by oxidation of the aldehyde with 25% nitric acid.

The following constants are cited in the literature for p-tolualdehyde and its derivatives [11]: b.p. 204°, $d_4^{16.7}$ 1.0187, $n_D^{16.6}$ 1.5470. The p-nitrophenylhydrazone has a m.p. of 200.5°, and the 2,4-dinitrophenylhydrazone has a m.p. of 232.5-234.5°. p-Toluic acid has a m.p. of 179°, 181°.

The constants of m-tolualdehyde and its derivatives differ sharply from the above [11].

From 4.5 g of 4-methyldihydrobenzaldehyde and a Grignard reagent (in 20% excess), we obtained an alcohol with the constants given in Table 2. The yield was 4.8 g (94%).

11.08 mg sub.: 31.82 mg CO_2; 10.63 mg H_2O. Found %: C 78.37; H 10.63. $C_9H_{14}O$. Calculated %: C 78.23; H 10.21.

On dehydration by distillation with a 10% solution of oxalic acid, the alcohol yielded a hydrocarbon:

B.p. 160-164°, d_4^{20} 0.8621, n_D^{20} 1.4935.

By means of a solution of bromine in acetic acid it was found that the substance contained about 13.5% of an unsaturated hydrocarbon. The aromatic hydrocarbon – p-methylethylbenzene – freed from the latter, had:

B.p. 160-162°, n_D^{20} 1.4950.

On oxidation with 25% nitric acid in sealed tubes, p-methylethylbenzene gave terephthalic acid, the dimethyl ester of which (and also a test sample of a mixture with the known preparation) melted at 140°.

In the literature almost identical constants [12] are cited for p-methylethylbenzene: b.p. 162°, n_D^{20} 1.4950.

SUMMARY

1. The homocyclization reaction of piperylene and isoprene with propargyl aldehyde was studied, whereby it was shown that the order of condensation corresponds to the electronic polarization of the components.

2. For the first time, the three isomers of methyldihydrobenzaldehyde were synthesized and some of its transformations were studied: dehydrogenation over sulfur, conversion to secondary alcohols by the action of the Grignard reagent, and reactions with hydrazine derivatives.

3. In two instances we studied the dehydration of the secondary 1,4-cyclohexadiene alcohols which occurs with the formation chiefly of aromatic hydrocarbons.

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* See Consultants Bureau Translation, page 73.

** See Consultants Bureau Translation, page 299.

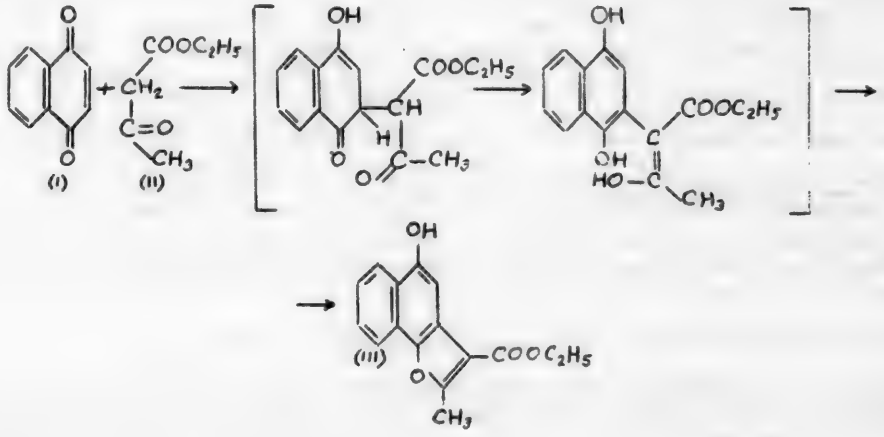
INVESTIGATIONS IN THE FIELD OF QUINONES

IV. [1]. SYNTHESIS OF SUBSTITUTED NAPHTHOFURANS

A. N. Grinev, V. N. Frosin and A. P. Terentyev

In 1892 Ikuta [2/ showed that p-benzoquinone, reacting with acetoacetic ester, gives a mixture of two substances – the diethyl ester of 2,6-dimethyl-benzo-(1,2-b;4,5-b')-difuran-3,7-dicarboxylic acid and the ethyl ester of 5-hydroxy-2-methyl-benzofuran-3-carboxylic acid. Later it was found that toluquinone also condenses with acetoacetic ester [3].

In our work it was found that, on reacting α-naphthoquinone (I) and acetoacetic ester (II) in the presence of zinc chloride, we obtained only one compound – the ethyl ester of 5-hydroxy-2-methylnaphthofuran-3-carboxylic acid (III). The yield was 79%.



Upon reaction of α-naphthoquinone (I) and benzoylacetic ester, we obtained the ethyl ester of 5-hydroxy-2-phenyl-naphthofuran-3-carboxylic acid (IV). The yield was 73%.

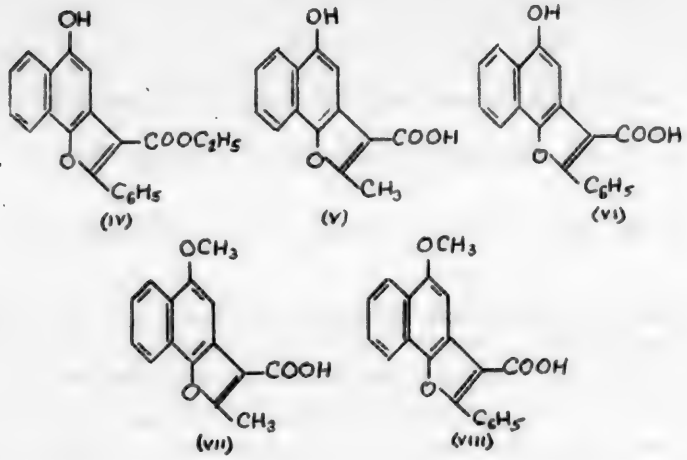
Under the same conditions, we carried out the condensation of α-naphthoquinone with both acetoacetic and benzoylacetic ester. The α-naphthoquinone and zinc chloride (as a 50% solution in anhydrous alcohol) were taken in equimolecular quantities, but the acetoacetic and benzoylacetic esters were taken in excess.

We carried out the reaction by heating on the water bath, during which α-naphthoquinone was added gradually to the other reactants. The selected conditions of carrying out the reaction were most favorable, since they almost completely eliminated resin formation.

Upon saponification of the esters III,(IV) with alcoholic alkali, we obtained the previously unknown hydroxy acids (V, VI). The methylation of the hydroxy acids with dimethyl sulfate led to the formation of the methoxy acids (VII, VIII). [See top of following page].

EXPERIMENTAL

The ethyl ester of 5-hydroxy-2-methyl-naphthofuran-3-carboxylic acid (III). Into a three-necked flask equipped with a stirrer and a reflux condenser, we poured a solution of 4.5 g (0.033 mole) of anhydrous zinc chloride in 5.7 ml of anhydrous ethyl alcohol and 15 ml (0.11 mole) of acetoacetic ester. To the mixture of the substances, by heating on the water bath and stirring, every 5 minutes we added by portions 5.2 g (0.033 mole) of α-naphthoquinone. The contents of the flask were heated for 25 minutes with stirring.



We cooled the reaction mass, separated the resulting crystals, washed them with ether and dried them. Their weight was 7.5 g; from the ether extract we separated 0.6 g of crystals. After 2 recrystallizations from ethyl alcohol, we obtained 7.1 g of the ester (III). The yield, based on quinone, was 79%. The m.p. was 209.5°.

Found %: C 70.98, 71.00; H 5.32, 5.31. $C_{16}H_{14}O_4$. Calculated %: C 71.10; H 5.22.

The ester was poorly soluble in acetone, benzene and dichloroethane; it was more soluble in ethyl alcohol.

4-Hydroxy-2-methyl-naphthofuran-3-carboxylic acid (V). We dissolved 9.45 g (0.035 mole) of the ester (III) in alcoholic alkali (6.8 g of sodium hydroxide in 100 ml of alcohol). We heated it until the sodium salt of the acid precipitated, then added 100 ml of water and boiled it, dissolving the salt. The acid was precipitated from the water-alcohol solution of the salt after boiling with activated carbon; the acid was recrystallized from 50% acetic acid. 7.7 g of crystals with a m.p. of 255-256° (decomposed) was obtained.

Found %: C 69.70, 69.73; H 4.44, 4.39. $C_{14}H_{10}O_4$. Calculated %: C 69.42; H 4.16.

5-Methoxy-2-methyl-naphthofuran-3-carboxylic acid (VII). We dissolved 4.1 g (0.017 mole) of 5-hydroxy-2-methyl-naphthofuran-3-carboxylic acid (V) in 20 ml of a 2 N solution of sodium hydroxide and added in several portions, with shaking, 3.8 ml (0.04 mole) of dimethyl sulfate. The mixture was refluxed for 1 hour. The resulting solution was cooled and acidified with hydrochloric acid. The acid which separated was recrystallized twice from glacial acetic acid. 3.9 g of the methoxy acid (VII) with a m.p. of 271-272 (decomposed) was obtained.

Found %: C 70.05, 70.09; H 4.67, 4.64; equiv 258. $C_{15}H_{12}O_4$. Calculated %: C 70.31; H 4.72; equiv 256.25.

The ethyl ester of 5-hydroxy-2-phenyl-naphthofuran-3-carboxylic acid (IV). The experiment was carried out under the same conditions as was the condensation of α-naphthoquinone with acetoacetic ester. In the experiment the following were taken: 4.3 g (0.027 mole) of α-naphthoquinone, 7 ml (0.04 mole) of benzoyl acetic ester, 3.75 g of zinc chloride and 4.7 ml of anhydrous ethyl alcohol. 6.75 g (73%) of the ester (IV) was obtained. The ester was poorly soluble in benzene and dichloroethane; it was soluble in ethyl alcohol. After recrystallization from ethyl alcohol, the yellow crystals had a m.p. of 180°.

Found %: C 75.88, 76.05; H 4.85, 4.84. $C_{21}H_{16}O_4$. Calculated C 75.90; H 4.85.

5-Hydroxy-2-phenyl-naphthofuran-3-carboxylic acid (VI). In the experiment 5.7 g of the ester (IV), 40 ml of ethyl alcohol, and 3 g of sodium hydroxide were taken. After recrystallization from 50% acetic acid, 4.3 g of the hydroxy acid (VI) with a m.p. of 236-238° was obtained.

Found %: C 74.75, 74.83; H 3.78, 3.87. $C_{19}H_{12}O_4$. Calculated %: C 74.99; H 3.98.

5-Methoxy-2-phenyl-naphthofuran-3-carboxylic acid (VIII). In the experiment 2.4 g of the hydroxy acid (VI), 20 ml of 2 N sodium hydroxide, and 1.9 ml of dimethyl sulfate were taken. The resulting methoxy acid (VIII)(1.94 g) was recrystallized from glacial acetic acid. The m.p. was 285-286°.

Found %: C 75.09, 75.17; H 4.23, 4.28. $C_{20}H_{14}O_4$. Calculated %: C 75.48; H 4.43.

SUMMARY

By condensations of α-naphthoquinone with acetoacetic and benzoylacetic esters we obtained the ethyl esters of 5-hydroxy-2-methyl-naphthofuran-3-carboxylic and 5-hydroxy-2-phenyl-naphthofuran-3-carboxylic acids. The hydroxy acids were obtained by saponification of the esters. The methoxy acids were obtained by methylation of the hydroxy acids.

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SYNTHESIS AND TRANSFORMATION OF METHYLDICYCLOHEXYLCARBINOL

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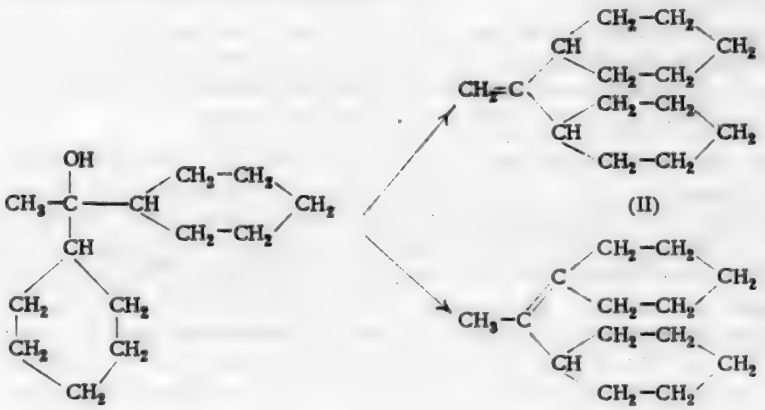
In a previous report we showed that methylcyclohexylcarbinol is dehydrated under the influence of concentrated sulfuric acid, with the formation of 1-phenyl-2-cyclohexyl-propene-1. It was of interest to investigate the dehydration of methyldicyclohexylcarbinol (I).

In the present case the liberation of water can be accomplished in two directions – toward the side of the formation of asymmetrical dicyclohexylethylene (II) and toward the formation of the isomeric compound with the heptacyclic double bond – methylcyclohexylcyclohexylidenemethane (III).



(I) (II) (III)

Whereas the mobility of the hydrogen atoms of the methyl group, in contrast to that of the hydrogen atoms of the methylene and methenyl groups, has been studied by many authors [2] by the dehydration of open-chain primary, secondary and tertiary alcohols, and has been quite clearly characterized by Butlerov [3], the problem concerning the dehydration of tertiary alcohols, which contain cyclic radicals, has been inadequately studied. This problem is of important practical value for the synthesis of the cyclic unsaturated compounds and their halogen derivatives, recently employed in the production of estrogens.

It should be mentioned that the behavior of the cyclohexyl radicals in the dehydration reactions of tertiary alcohols also formerly attracted the attention of a number of investigators. Auwers and Ellinger [4], on dehydration of dimethylcyclohexylcarbinol, obtained a mixture of hydrocarbons of the composition C_9H_{16}, the structure of which remained undemonstrated. Perkin and Macubara [5] and other authors, by dehydration of the same carbinol with potassium bisulfate, likewise contributed no clarity to this reaction. Interesting data were obtained by English, Russel and Brutcher [6] by the dehydration of methylcyclohexylphenylcarbinol (close in structure to our tertiary alcohol). Upon dehydration of methylcyclohexylphenylcarbinol, they obtained 1-cyclohexyl-1-phenylethylene and methyl-cyclohexylidene-phenylmethane. The structure of the hydrocarbons which they obtained was demonstrated by oxidation; in one case phenyl cyclohexyl ketone was observed, in the second instance acetophenone was observed.

Methyldicyclohexylcarbinol, obtained for the first time by Venus-Danilova from methylmagnesium iodide and dicyclohexyl ketone, on dehydration with a 10% solution of oxalic acid, gave asymmetrical dicyclohexylethylene (b.p. 140° at 18 mm) [7]. The structure of the hydrocarbon was not demonstrated by oxidation. It was demonstrated indirectly by study of the isomerization products of the oxide of the dicyclohexylethylene.

We carried out the synthesis of methyldicyclohexylcarbinol from methyl cyclohexyl ketone and cyclohexylmagnesium bromide in ether by heating on a water bath. Two fractions were separated as a result of vacuum distillation of the product at 5 mm, in the presence of concentrated sulfuric acid: 134-135° and 166-167°. The substance boiling at 134-135° (5 mm) corresponded exactly to the hydrocarbon described by Venus-Danilova. By oxidation with potassium

permanganate, we separated the dicyclohexyl ketone which was characterized by a semicarbazone with a m.p. of 197-198° (decomposed). The second substance, on oxidation by potassium permanganate, yielded methyl cyclohexyl ketone, which was characterized by a semicarbazone with a m.p. of 170-171°. Moreover, from the oxidation products cyclohexenone was obtained as the semicarbazone.

The oxidation products of the isomeric hydrocarbons substantiated their structure: the 1st fraction corresponded to asymmetrical dicyclohexylethylene (II), and the 2nd corresponded to methyl-cyclohexyl-cyclohexylidene-methane (III).

An evolution of hydrogen bromide was observed on bromination (in chloroform) of the unsaturated hydrocarbons. The resulting brominated derivatives contained (according to analysis) one atom of bromine per molecule. Apparently, here the addition of two atoms of bromine at the ethylene bond occurred, but was followed by the liberation of hydrogen bromide.

EXPERIMENTAL

Methyldicyclohexylcarbinol

25.2 g of methyl cyclohexyl ketone with a b.p. of 68° (12 mm), in a twofold volume of anhydrous ether, was added to cyclohexylmagnesium bromide, prepared from 32.6 g of magnesium in anhydrous ether (the Grignard reagent was taken in 20% excess). The reaction was carried out by heating on a water bath. After addition of the total quantity of the ketone, the reaction mixture was heated 4 hours more, with stirring.

On the next day, the reaction mixture was decomposed with water, then with 5% sulfuric acid, and was extracted with ether. The ether extract was dried over sodium sulfate, and after removal of the ether the reaction product was vacuum distilled. During the distillation process drops of water appeared on the walls of the distillation flask. The following fractions were separated: 57-100° (5 mm) – about 6 g (unreacted methyl cyclohexyl ketone, m.p. of the semicarbazone 171-172°) and 130-170° (5 mm) – 17.5 g. About 4 g of resin remained in the flask. The substance obtained was a light yellow liquid of pleasant odor, which decolorized bromine water and a solution of potassium permanganate. After addition of 5 drops of concentrated sulfuric acid, the product was distilled again. We separated about 6 g of a colorless liquid, b.p. 134-135° (5 mm), and 9 g of the liquid of light-yellow color, b.p. 166-167° (5 mm). Both liquids were insoluble in water, but highly soluble in alcohol, ether and chloroform, and decolorized bromine water and a solution of potassium permanganate.

Because not all of the ketone reacted, a repetition of the synthesis was carried out with a 25-30% excess of cyclohexylmagnesium bromide, but in all cases about 20% of unreacted ketone was recovered. The total yield of the ethylene product was 56% (from calculation on the basis of the ketone reacting): 6 g (22.4%) with a b.p. of 134-135° (5 mm) and 9 g (33.6%) with a b.p. of 166-167° (5 mm).

Analysis of the substance with a b.p. of 166-167° (5 mm): d_4° 0.9735, d_{20}^{20} 0.9715.

0.0922 g sub.: 0.2956 g CO_2; 0.1001 g H_2O. 0.0875 g sub.: 0.2798 g CO_2; 0.0976 g H_2O. Found %: C 87.49, 87.27; H 12.15, 12.48. $C_{14}H_{26}$. Calculated %: C 87.5; H 12.0.

Bromometric determination of the double bond in the hydrocarbon which had a b.p. of 166-167° (5 mm). We dissolved a weighed portion of the substance in 10 ml of alcohol, added an excess of a titrated alcoholic solution of bromine, the titre of which was found for each experiment with a 0.1 N solution of sodium thiosulfate, and allowing the solution to stand for 10 minutes, added a 50% solution of potassium iodide. The iodine which was liberated was back-titrated with sodium thiosulfate.

0.2458 g sub: 0.2072 g Br. 0.6203 g sub.: 0.5263 g Br. $C_{14}H_{26}$. Calculated: 0.2048, 0.5169 g Br.

The ether-soluble dibromide was a dark-green, resinous substance. In order to purify the ether solution, we cautiously refluxed it with carbon on the water bath. The filtrate, after removal of the ether, was a viscous, dark-green liquid.

Oxidation of the hydrocarbon $C_{14}H_{26}$ which had a b.p. of 166-167° (5 mm). 2 g of the substance in 20 ml of ether was oxidized by a 2% solution of potassium permanganate (105 ml), in the cold, with vigorous stirring. The manganese dioxide precipitate was filtered off, washed with water, and then refluxed with ether on the water bath; after removal of the ether the residue, which had the characteristic odor of methyl cyclohexyl ketone, was treated with a semicarbazide solution. The semicarbazone, recrystallized from alcohol, melted at 171-172°, and no m.p. depression was observed for a test sample of a mixture with the known semicarbazone of methyl cyclohexyl ketone. The hydrous liquid was neutralized, concentrated and treated with ether. After removal of the ether, the residue was treated with a semicarbazide solution; thus, we obtained a semicarbazone which, after recrystallization from alcohol, melted at 165-167°,

and in a mixture with the known semicarbazone of cyclohexanone no depression of the melting point was observed.

Bromometric determination of the double bond in the substance which had a b.p. of 131-135° (5 mm): d_4^{20} 0.9246, d_{20}^{20} 0.9104.

0.2104 g sub.: 0.1755 g Br. 0.3419 g sub.: 0.2971 g Br. $C_{14}H_{24}$. Calculated: 0.1753, 0.2935 g Br.

Oxidation of the hydrocarbon $C_{14}H_{24}$ which had a b.p. of 134-135° (5 mm). 2 g of the substance was dissolved in 20 ml of ether, and with energetic stirring was oxidized in the cold by potassium permanganate (210 ml). The manganese dioxide precipitate was filtered off, washed with water, and after drying was refluxed with ether on the water bath. After removal of the ether, about 0.5 g of an oily liquid of pleasant odor remained, which was converted to the semicarbazone by a solution of semicarbazide. The semicarbazone, after two recrystallizations from alcohol, melted at 198-200° (decomposed), and with respect to all its properties corresponded to the semicarbazone of dicyclohexyl ketone. We were unable to detect formic acid in the hydrous liquid.

Bromination of the hydrocarbon $C_{14}H_{24}$ which had a b.p. of 134-135° (5 mm). To 4 g of the substance in 20 ml of chloroform, we added 3.2 g of bromine in 10 ml of chloroform. We observed some evolution of heat, and a strong liberation of hydrogen bromide, from the mixture. On the next day, after removal of the chlofoform, a dark, viscous liquid remained. The latter was extracted with ether, purified by cautious refluxing on the water bath in the presence of activated carbon, and filtered. The filtrate was dried with sodium sulfate. After removal of the ether, 4.4 g of a greenish, viscous liquid remained; it was insoluble in water and alcohol, but highly soluble in ether and chloroform.

0.4814 g sub.: 18.45 ml 0.1 N solution $AgNO_3$ (according to Stepanov). 0.5032 g sub.: 19.05 ml 0.1 N solution $AgNO_3$. Found %: Br 30.6, 30.25. $C_{14}H_{23}Br$. Calculated %: Br 29.52.

Bromination of the hydrocarbon $C_{14}H_{24}$ which had a b.p. of 166-167° (5 mm). 4 g of the substance in 20 ml of chloroform was subjected to bromination and further treatment similar to the preceding; thus, the liberation of hydrogen bromide was observed. The purified product was a still more viscous, dark-cinnamon colored liquid, which did not withstand heat, and was soluble in ether and chloroform.

0.7818 g sub.: 29.3 ml 0.1 N solution $AgNO_3$ (according to Stepanov). Found %: Br 29.94. $C_{14}H_{23}Br$. Calculated %: Br 29.52.

SUMMARY

1. Methyldicyclohexylcarbinol was synthesized from methyl cyclohexyl ketone and cyclohexylmagnesium bromide.

2. On dehydration of methyldicyclohexylcarbinol by heating in the presence of concentrated sulfuric acid, two isomeric unsaturated hydrocarbons were formed—asymmetrical dicyclohexylethylene and methyl-cyclohexyl-cyclohexylidene-methane.

3. The structure of the hydrocarbons obtained was established by means of their cleavage by oxidation.

4. The replacement of one atom of hydrogen by bromine was brought about by the action of bromine on the ethylene hydrocarbons in a solution of chloroform.

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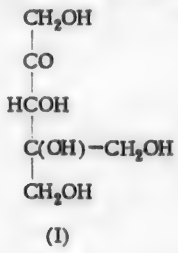
THE ISOMERIC DIACETONE DERIVATIVES OF DENDROKETOSE

L. M. Utkin

A few years ago the author of this article showed [1] that the condensation of dihydroxyacetone, in an alkaline medium (0.05 N NaOH), proceeds in the main without its preliminary epimerization to glyceraldehyde, and leads to the formation of a ketohexose with a branched hydrocarbon chain, 4-hydroxymethyl-2-ketopentose, which has received the name of dendroketose (I); the latter is the substance which E. Fischer named "β-acrose", and which previously was erroneously identified with dl-sorbose.



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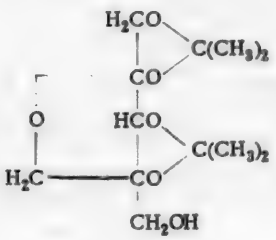

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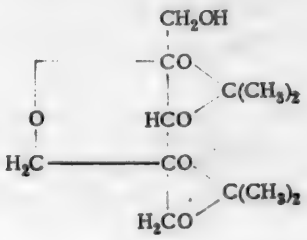


(III)

By means of biochemical decomposition of one of the antipodes from the racemic form, optically-active dextrorotatory dendroketose and its derivatives were obtained, which enabled us to demonstrate its structure and the d-configuration of its third carbon atom, which was the only center of asymmetry of the keto form of this sugar; this was accomplished by shortening the carbon chain of the dendroketose by 1 C_1 atom, as a result of which crude d-apionic acid was obtained. Determination of the structure and configuration of dendroketose was achieved by the study of the transformations of its 1,2;3,4-diacetone derivative (II) which was isolated in the crystalline form.

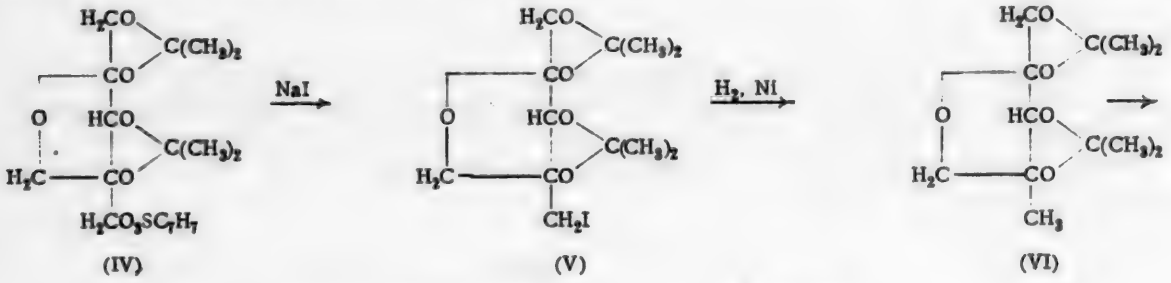
The yield of the racemic form of this derivative did not exceed 20% of the theoretical, based on the dihydroxyacetone taken, and it constituted about half of the total quantity of the diacetone-derived fraction, obtained with the acetonized products of the condensation of dihydroxyacetone. The remaining portion of this fraction consisted of a non-crystallizing syrup, which remained non-crystalline after its benzoylation. On the assumption that it might contain the isomeric diacetone derivative, we subjected it to tosylization in pyridine, after which we were able to separate from it, in a yield of about 5% of the theoretical, based on the dihydroxyacetone, the crystalline p-toluenesulfonate of the isomeric diacetone hexose. By splitting off the tosyl group with sodium amalgam in a water-alcohol solution [2], we obtained its isomeric diacetonedendroketose, which gave a characteristic violet coloration for the Seliwanoff reaction. Unlike the previously described diacetone derivative (II), which had a strong levorotation ($[\alpha]_D$ −121°), the isomeric derivative showed a dextrorotation ($[\alpha]_D$ + 60.5°). Oxidation of the isomeric diacetone derivative by permanganate in an alkaline medium yielded diacetoneketohexonic acid, which formed a more crystalline potassium salt than did the earlier described [1] acid, the potassium salt of which did not crystallize. On acidification of the aqueous solution of the potassium salt, the acid immediately precipitated as short prisms of the hydrate. After the acid was heated with 20 parts of water on a boiling water bath for 1.5 hours, the solution showed a combination of iodine in the acid medium, in a quantity which corresponded to a 7% rearrangement to the isomeric ascorbic acid. It was concluded that the acid was diacetone 2-ketohexonic acid, and that the isomer of the diacetonedendroketose separated has a free primary hydroxyl group in position 1, i.e., is the 2,3;4,5'-diacetone derivative (III).

It is interesting to note that the acid which was studied, 4-hydroxymethyl-2-ketopentonic acid, showed a relatively small degree of rearrangement, whereas the 2-ketopentonic acid rearranged very readily to the corresponding ascorbic acid [3].

It is known that the 1-p-tosylacetone derivative of the ketose either does not react with sodium iodide [4], or reacts with difficulty [5], whereas the derivative with the p-tosyl group substituted in position 5 of the ketopentoses or in position 6 of the ketohexoses, is readily converted to the analogous acetone derivative of the corresponding iodohydrins. We verified this principle for the p-tosylsulfonates of the two diacetone derivatives of dendroketose.

5'-p-Tosyl-1,2;3,4-diacetonedendroketose (IV) was prepared by the action of p-tolylsulfochloride on the previously described [1] diacetonedendroketose (II) in pyridine. The reaction of this substance with sodium iodide was

carried out in a medium of boiling n-butanol; replacement of the acetone, usually employed as the solvent in this reaction, by n-butanol enabled us to dispense with the use of a sealed tube. The reaction took place rapidly, and in 1 hour the theoretical quantity of sodium p-tolylsulfonate had separated. After treatment of the solution, 5'-iodo-5'-desoxy-1,2;3,4-diacetonedendroketose (V) was obtained. The catalytic dehalogenation of this substance gave diacetonedendroketomethylose (VI), from which crystalline dendroketomethylose (VII) was obtained by hydrolysis. In the Selivanoff reaction it gave a pure blue coloration.

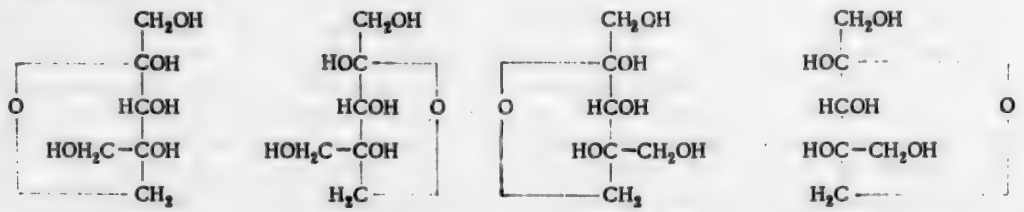


(IV) (V) (VI)

(VII) (VIII)

The 1-p-tosyl derivative (VIII), in the form of which the isomeric diacetonedendroketose (III) separated, even on a 5-hour heating with sodium iodide in a medium of boiling n-butanol gave no traces of the separation of sodium tolylsulfonate; and conversely, from the solution, the original substance was obtained almost quantitatively.

These experiments showed that the p-tolylsulfonates of the two isomeric diacetone derivatives of dendroketose behave in accordance with the principle given above, and confirmed the structure of the compound (VII), and consequently, also of (III).



(IX) (X) (XI) (XII)

A peculiarity of the structure of dendroketose includes the fact that, on formation of the cyclic form of the molecule, two new centers of asymmetry arise — C_3 and C_4, whereas for the normal ketohexose only one arises — C_5; therefore, the existence of 8 stereoisomers of the cyclic form of dendroketose are possible, considering all the antipodes, or 4 stereoisomers are possible considering one series.

Taken in pairs in the order of the arrangement of the formulas, these 4 configurations are the α- and β-forms of the two diastereoisomers, which differ by the configuration of the C_4 atom. All 4 stereoisomers should give the same phenylosazone, since on formation of the osazone the cyclic structure of the molecule is converted to a chain structure, and the asymmetry not only of the 2nd, but also of the 4th carbon atom, disappears. The arrangement of the primary hydroxyl groups in relation to the hydroxyl groups of the terminal part of the molecule permits all four stereoisomers to form the diacetone derivative; thus, the stereoisomer (IX) may form both the 2,3;4,5'-and the 1,2;3,4-diacetonehexose; thus, the isomeric diacetone derivatives (II) and (III), which we isolated, may be the derivatives of the stereoisomer (IX). However, it is more likely that they are the derivatives of stereoisomers (X) and (XI), respectively, since the great difference in their specific rotations (−121° and + 60°) could hardly be the result of simple transformation of the isopropylidene group; in principle the difference should lie in the configuration of their sugar molecule.

EXPERIMENTAL*

Condensation of Dihydroxyacetone and Separation of the Optically-active Diacetonedendroketose (II)

25 g of dihydroxyacetone was dissolved in 475 ml of water, and 25 ml of 1 N NaOH was added. After 4 hours at 25°, the dark-yellow solution was neutralized with 6 N sulfuric acid, and 2.5 g of $NH_4H_2PO_4$, 0.3 g of KCl, 0.25 g of $MgSO_4 \cdot 7H_2O$, and 0.05 g of $ZnSO_4 \cdot 7H_2O$ were added; thin layers of the solution were poured into Erlenmeyer flasks with cotton plugs, and were boiled and sown with a Penicillium culture. After 10 days $\alpha + 0.47°$ (constant) was obtained. The solution was purified with lead acetate and evaporated in vacuo to a syrup, which was dried to constant weight over sulfuric acid and sodium hydroxide in a vacuum-desiccator; the yield was 15 g. We acetonized 300 ml of acetone with 12 ml of sulfuric acid (d 1.84) at 35°; all of it passed into solution in 2 hours, after which it was left at room temperature for a day, and then the solution was neutralized by stirring with 30 g of anhydrous soda. We distilled the acetone from the filtrate (toward the end distillation in vacuo), the remaining syrup was extracted several times with ether, and the ether extract was washed with a 20% solution of potassium carbonate; the latter was extracted with fresh ether, and the combined ether extracts were dried by sulfate; after the ether was driven off, the residue was vacuum distilled (10.1 g), and had a b.p. of 115-130° (2 mm). The distillate (7.4 g) was a viscous, yellowish oil, and it soon crystallized as thin prisms.

a) Separation of (II) as the benzoyl derivative. The distillate was dissolved in 35 ml of pyridine, and 4.5 ml of benzoyl chloride was added to the solution; after a day the mixture was poured into 500 ml of water. The oil which separated soon partially crystallized; the viscous mass was collected on a glass filter and washed with 30 ml of methanol. 2.8 g (11%, considering that half of the sugar was consumed by the mold) was obtained. After recrystallization from hot methanol, its m.p. was 97°.

0.1737 g sub.: α −1.12°; $[\alpha]_D^{18}$ −64.5° (c 1.7, acetone).

0.1405 g sub.: saponified by 0.1 N alcoholic KOH. Combined 3.84 ml. Found %: C_6H_5CO 28.74. $C_{19}H_{24}O_7$. Calculated %: C_6H_5CO 28.85.

Saponification. 1.5 g of the benzoyl derivative was treated with a solution of 0.08 g of sodium in 15 ml of methanol; after 1 hour the methanol was vacuum distilled, 30 ml of water was added and distilled, the residue was extracted with ether, and the extract was dried with sulfate; after removal of the ether an oil remained, which crystallized at once (1.05 g) on cooling. It was recrystallized from 5 ml of gasoline (b.p. 85-120°). The thin prisms, 0.85 g, had a m.p. of 89°.

0.1192 g sub.: α −1.44°; $[\alpha]_D^{18}$ −120.9° (c 1.2, acetone).

3.246 mg sub.: 6.570 mg CO_2, 2.260 ml H_2O. 3.428 mg sub.: 7.004 mg CO_2; 2.349 mg H_2O. Found %: C 55.20, 55.72; H 7.78, 7.67. $C_{12}H_{22}O_8$. Calculated %: C 55.37; H 7.75.

b) Separation by direct treatment of the distillate. The crystallizing distillate (6.7 g) was dissolved by warming it in 4 ml of gasoline; after a day crystals separated, and were washed with gasoline and dried. The yield was 1.7 g (9.5%) and the m.p. was 89°.

The production of the dl-form of derivative (II) was accomplished by the same method, excluding the stage of reaction of the mold in the solution of the condensation products; thus, the yield of the benzoyl derivative amounted to 21%, and the m.p. was 120-121°. The same direct treatment of the distillate gave a yield of 10% of the diacetone derivative (II); the m.p. was 84-85°, and the b.p. was 111-112° (2 mm). It sublimed at 90° (10 mm).

5'-p-Tosyldiacetonedendroketose (IV)

0.6 g of the diacetone derivative (II) in 5 ml of pyridine and 0.5 g of p-tosylchloride were used. After a day it was diluted with water, extracted with ether and treated by the usual method; the syrup crystallized when 1 ml of methanol was added. The yield was 0.85 g; the thin prisms from methanol had a m.p. of 101-101.5°. (The dl-form had a m.p. of 91.5-92°).

0.1101 g sub.: α −0.82°; $[\alpha]_D^{18}$ −74.5° (c 1.1, acetone).

7.725 mg sub.: 4.360 mg $BaSO_4$. 8.535 mg sub.: 5.355 mg $BaSO_4$. Found %: S 7.74, 7.71. $C_{19}H_{26}O_9S$. Calculated %: S 7.74.

* In determination of the angles of rotation, the length of the tube was equal to 1 dm, and the volume of the solutions was 10 ml.

1-p-Tosyl-2,3;4,5'-diacetonedendroketose (VIII)

The mother liquor, after separation of the benzoyl derivative of optically active diacetonedendroketose (II), was evaporated in vacuo, and the residue was extracted with ether; the viscous yellow syrup which remained after removal of the ether was saponified with a solution of 0.5 g of sodium in 50 ml of methanol; after a day the methanol was removed in vacuo, 50 ml of water (for removal of the methyl benzoate) was added and vacuum distilled, and the residue was extracted with ether. After the ether was driven off, 5.5 g of a mixture of the isomeric diacetone derivatives remained, which was dissolved in 30 ml of pyridine and treated with 4.5 g of tosylchloride (120% of the theoretical). After a day, the mass was diluted with water, and the oil which separated was extracted with ether; after the usual treatment of the extract, a syrup (8.5 g) was obtained, and it was dissolved in 8.5 ml of methanol; in the standing solution, needles were precipitated in a yield of 2.1 g; after recrystallization from methanol they had a m.p. of 112°, after which the melt solidified at once and a second time melted at 119.5-120°. From gasoline or n-butanol the short prisms had a m.p. of 119.5-120°. Both substances had the same composition and the same specific rotation. (The dl-form was deprived of its dimorphism; the thick, short needles had a m.p. of 90.5-92°).

0.2093 g sub.: α + 0.27°; $[\alpha]_D^{18}$ + 12.9° (c 2.1, acetone).

3.793 mg sub.: 7.665 mg CO_2; 2.050 mg H_2O. 3.992 mg sub.: 8.064 mg CO_2; 2.202 mg H_2O. Found %: C 55.11, 55.09; H 6.05, 6.17. $C_{19}H_{26}O_8S$. Calculated %: C 55.06; H 6.32.

2,3;4,5'-Diacetonedendroketose (III)

1 g of the p-tosyl derivative (VIII) was dissolved in 50 ml of 80% alcohol and, with mechanical stirring, 25 g of 2% sodium amalgam was added; after 3 hours, 25 g more of the amalgam was introduced and stirring was continued for 8 hours. The solution was poured off from mercury, neutralized with hydrochloric acid (to phenolphthalein) and evaporated in vacuo; the residue was treated with 10 ml of a 20% solution of potassium carbonate and extracted with ether; after drying with sulfate and driving off the ether, 0.6 g of a syrup, which crystallized in the desiccator, was obtained. The crystals were dissolved in 6 ml of hot gasoline, and the solution was treated with carbon; on cooling, lustrous, friable needles with a m.p. of 63.5-64.5° separated; they strongly reduced Fehling solution after hydrolysis by acid. (The dl-form was obtained as a non-crystallizing syrup).

0.0925 g sub.: α +0.56°; $[\alpha]_D^{17}$ + 60.5° (c 0.9, acetone).

4.256 mg sub.: 8.637 mg CO_2; 2.899 mg H_2O. Found %: C 55.34; H 7.62. $C_{12}H_{20}O_6$. Calculated %: C 55.37; H 7.75.

The phenylosazone of dl-dendroketose. The syrupy dl-form of the diacetone derivative (III), obtained from 0.5 g of the p-tosyl derivative (VIII) (dl) by the method described, was heated with 10 ml of 0.3 N sulfuric acid on a boiling bath for 30 minutes; the solution was neutralized with sodium hydroxide, and 0.5 g of the phenylhydrazine hydrochloride and 0.7 g of sodium acetate were added to it, and the mixture was heated on a boiling bath for 3 hours. After washing the osazone with ether, and after reprecipitation by petroleum ether from a solution in acetone, and after recrystallization from 5 ml of 20% alcohol, narrow light-yellow plates with a m.p. of 155-157° were obtained; it gave no m.p. depression with the known phenylosazone of dendroketose (I).

Potassium Salt of 2,3;4,5'-diacetone-2-ketohexonic Acid

To a solution of 1.2 g of the diacetone derivative (III) in 100 ml of 1% KOH, 50 ml of a 1% solution of permanganate was added, with stirring for 1 hour. After a day, the bluish-green solution was decolorized with H_2O_2, and the MnO_2 was filtered off and washed with hot water, the filtrate was neutralized with sulfuric acid (to phenolphthalein) and evaporated to dryness in vacuo; the salt was digested with 60 ml of boiling anhydrous alcohol. After concentration of the solution to 15 ml, the precipitation of fine needles began and was completed by the addition of 15 ml of ether; the yield of the salt was 0.6 g; it was recrystallized from 20 ml of boiling anhydrous alcohol.

0.1070 g sub.: α + 0.50°; $[\alpha]_D^{16}$ + 46.7° (c 1.1, water).

0.1053 g sub.: 0.0293 g K_2SO_4. Found %: K 12.53. $C_{12}H_{17}O_7K$. Calculated %: K 12.49.

2,3;4,5'-Diacetone-2-ketohexonic Acid

To a chilled solution of 0.5 g of the K-salt in 5 ml of water, 3 ml of 1 N hydrochloric acid was added; short prisms separated at once. After separation of the crystals, washing with cold water and drying in a vacuum-desiccator, the yield was 0.3 g, and the m.p. was 96-97°. (The dl-form melted at 85-86°).

0.1155 g sub.: α + 0.65°; $[\alpha]_D^{18}$ + 56.3° (c 1.2, acetone).

3.457 mg sub.: 6.244 mg CO_2; 2.032 mg H_2O. 3.153 mg sub.: 5.674 mg CO_2; 1.876 mg H_2O. Found %: C 49.26, 49.08; H 6.58, 6.66. $C_{12}H_{18}O_7 \cdot H_2O$. Calculated %: C 49.31; H 6.90.

5'-Iodo-5'-desoxy-1,2;3,4-diacetonedendroketose (V)

1 g of the p-tosyl derivative (IV), 1 g of sodium iodide and 10 ml of n-butanol were heated in an oil bath at 120-125°, in a wide test tube with an inverted tube. After 20 minutes the separation of plates of sodium p-tolylsulfonate began; after 1 hour the solution was cooled and diluted with 30 ml of acetone, and 0.45 g (96%) of the salt separated. The solution was evaporated in vacuo, the residue was diluted with water, extracted with ether, and the extract was washed with a solution of thiosulfate; after drying with sulfate and driving off the ether, an oil which quickly crystallized, remained; 0.75 g (83%) of the crystals was obtained. They were recrystallized from 7.5 ml of 70% methanol; the resulting rhombic plates had a m.p. of 41.5-42°. (The dl-form melted at 53-54°).

0.1282 g sub.: α −1.14°; $[\alpha]_D$ −88.9° (c 1.3, acetone).

6.532 mg sub.: 1.061 ml 0.01 N $Na_2S_2O_3$. Found %: I 34.35. $C_{12}H_{19}O_5I$. Calculated %: I 34.29.

1,2;3,4-Diacetonedendroketomethylose (VI)

1.2 g of diacetoneiodohydrin (V) was hydrogenated in 25 ml of a 1% solution of sodium hydroxide in methanol, with 1.5 g of a paste of skeletal nickel. Absorption of the calculated quantity of hydrogen was completed in 20 minutes. After separation of the catalyst, neutralization and driving off of the methanol, the reaction product was extracted with ether. The yellowish oil was distilled; its b.p. was 74-75° (4 mm); the yield was 0.6 g (75%).

0.1037 g sub.: α −1.23°; $[\alpha]_D^{17}$ −118.6° (c 1.0, acetone).

3.935 mg sub.: 8.596 mg CO_2; 2.920 mg H_2O. Found %: C 59.30; H 8.30. $C_{13}H_{20}O_5$. Calculated %: C 58.99, H 8.25.

Dendroketomethylose (VII)

0.5 g of the diacetone derivative (VI) and 10 ml of 0.1 N sulfuric acid were heated on a boiling water bath for 2 hours; the hydrolyzate was neutralized with barium carbonate and evaporated over sulfuric acid in a vacuum-desiccator. The resulting syrup was treated with 1 ml of anhydrous alcohol, after which it began to crystallize as plates; the crystals were triturated with 3 ml of anhydrous alcohol, separated, washed and dried. We obtained 0.16 g of a substance with a m.p. of 119-120°. It strongly reduced Fehling solution on heating.

0.1031 g sub.: α + 0.05°; $[\alpha]_D$ + 5° (c 1.0 water).

3.369 mg sub.: 5.400 mg CO_2; 2.200 mg H_2O. Found %: C 43.71; H 7.31. $C_6H_{12}O_6$. Calculated %: C 43.89; H 7.37.

Reaction of 1-p-Tosyldiacetonedendroketose (VIII) with Sodium Iodide

0.5 g of the optically-active compound (VIII), 0.5 g of sodium iodide and 5 ml of n-butanol were boiled for 5 hours, as described above. The solution remained clear. After removal of the solvent, 0.5 g of the original substance was obtained.

SUMMARY

1. It was shown that the fraction of the diacetone derivative which was obtained by acetonization of the condensation products of dihydroxyacetone contains both the 1,2;3,4-diacetonedendroketose described earlier and the isomeric diacetone derivative of the same sugar.

2. The structure of the new isomer was demonstrated to be 2,3;4,5'-diacetonedendroketose by the formation, during its oxidation, of diacetone-2-ketohexonic acid, and by the absence of the reactivity of its p-tosyl derivative toward sodium iodide.

3. It was found that 5'-p-tosyl-1,2;3,4-diacetonedendroketose reacts readily with sodium iodide with the formation of 5'-iodo-5'-desoxydiacetonedendroketose, from which we obtained the diacetone derivative of dendroketomethylose and its dendroketomethylose — a representative of the hexomethyloses with branched carbon chains.

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REACTIONS OF THE METAL HALIDE-ALCOHOLATES

II. REACTION OF MAGNESIUM HALIDE-ALCOHOLATES OF THE PRIMARY-AROMATIC, SECONDARY AND TERTIARY ALIPHATIC-AROMATIC ALCOHOLS WITH ESTERS

I. I. Lapkin

In order to elucidate the effect of the structure of the carbinolate radicals, and also the effect of the character of the esters, on the course of the reaction, we studied the reactions of the carbinolates of the primary aromatic, secondary alkylarylcarbinols and tertiary-dialkylarylcarbinols with esters.

It was found that, on reaction with esters, the magnesium halide-alcoholates of benzyl alcohol, unlike the alcoholates of the secondary aromatic alcohols [1], form not only benzyl halides, but also benzyl esters.

With formates and oxalates, the magnesium bromide alcoholates of the secondary aliphatic-aromatic alcohols form both halide derivatives ($R-CHBr-CH_2R'$) and unsaturated hydrocarbons ($R-CH=CH-R'$); the hydrocarbons seem to be almost the sole reaction products of the magnesium halide alcoholates of the tertiary dialkylarylcarbinols. Finally, by the action of diethyl oxalate on the magnesium halide bornylates, only esters (the ethyl bornyl and the dibornyl ester of oxalic acid) are formed.

The results of the experiments are cited in Table 1.

TABLE 1

Expt. No.	Components reacting	Composition of the reaction products (in %)			
		halide	carbinol	ester	unsaturated hydrocarbon
1	MgBr-phenylcarbinolate + ethyl formate	49	27	24	–
2	MgI-phenylcarbinolate + ethyl formate	49	13	38	–
3	MgBr-phenylcarbinolate + diethyl oxalate	55	20	25	–
4	MgI-phenylcarbinolate + diethyl oxalate	56	18	24	–
5	MgCl-phenylcarbinolate + diethyl oxalate	11	32	57	–
6	MgBr-phenylcarbinolate + diethyl malonate	–	–	100	–
7	MgI-phenylcarbinolate + diethyl malonate	4	–	96	–
8	MgBr-phenylcarbinolate + diethyl succinate	3	6	91	–
9	MgI-phenylcarbinolate + diethyl succinate	7	9	84	–
10	MgBr-n-butylphenylcarbinolate + ethyl formate	56	44	–	–
11	MgBr-n-butylphenylcarbinolate + diethyl oxalate	52	21	–	27
12	MgBr-propyl-α-naphthylcarbinolate + diethyl oxalate	22	21	–	57
13	MgBr-dimethylphenylcarbinolate + ethyl formate	20	–	–	80
14	MgBr-diethylphenylcarbinolate + ethyl formate	10	–	–	90
15	MgBr-bornylate + diethyl oxalate	–	10	90	–
16	MgI-bornylate + diethyl oxalate	–	8	92	–

As was shown earlier [1], diarylmethyl halides are formed by the reaction of the magnesium halide-diarylcarbinolates. Attempts to use this reaction for alkoxyl-containing phenylnaphthyl- and dinaphthylcarbinolates, namely, the MgBr-carbinolates of phenyl-(2-methoxynaphthyl-1)-carbinol, phenyl-(2-ethoxynaphthyl-1)-carbinol, di-(2-methoxynaphthyl-1)-carbinol and di-(2-ethoxynaphthyl-1)-carbinol, did not lead to the formation of the halides, because of the very low solubility of the magnesium halide-carbinolates in anhydrous ether. We succeeded only in the case of the conversion of magnesium bromide-di-(2-methoxynaphthyl-1)-carbinolate to di-(2-methoxynaphthyl-1)-methyl ether by the action of diethyl oxalate.

TABLE 2

Test no.	Name of alcohol	Starting material for synthesis	Yield (in %)	Property	Content (in %) C found	C calculated	H found	H calculated	OH found	OH calculated	OR found	OR calculated
1	propyl-α-naphthylcarbinol	α-naphthylmagnesium bromide + butyraldehyde	–	B.p. 133-134° (3 mm) d_4^{20} 1.0710, n_D^{20} 1.5992, MR_D 63.90, cal. 61.64	83.80	83.96	7.99	8.05	8.5	8.5	–	–
2	phenyl-(2-ethoxynaphthyl-1) carbinol	β-ethoxynaphthylmagnesium bromide + benzaldehyde	40	m.p. 180-181°	81.78	81.99	6.48	6.51	5.7	6.1	15.5	16.1
3	di-(2-methoxynaphthyl-1)-carbinol	β-methoxynaphthylmagnesium bromide + ethyl formate	50	m.p. 154°	80.24	80.21	5.78	5.65	4.4	4.9	16.7	18.0
4	di-(2-ethoxynaphthyl-1)-carbinol	β-ethoxynaphthylmagnesium bromide + ethyl formate	78	m.p. 157°	80.37	80.59	6.56	6.50	4.1	4.5	22.1	24.2

EXPERIMENTAL*

The reaction between the magnesium halide-alcoholates and the esters was carried out under conditions described earlier [1]. In the mixture of products obtained, the content of the halide derivatives was determined either by means of an alcoholic solution of silver nitrate or by the Stepanov method; the carbinol content was measured by a determination of the hydroxyl by the Chugaev-Tserevitinov or Terentyev method, the ester contents were determined by saponification of the reaction products with a titrated water-alcohol solution of potassium hydroxide. In the latter determination, we naturally considered the quantity of titrated solution which was consumed for the saponification of the halide.

From the difference between 100% and the sum of the halide, carbinol and ester contents, the content of the unsaturated hydrocarbons, which were identified in experiments 3 and 4, was determined. The results of the investigations are presented in Table 1.

The carbinols, which were required for the experiments, and which had not been described earlier in the literature, were synthesized under the usual conditions of the Grignard synthesis. Their properties are presented in Table 2.

Synthesis of di-(2-methoxynaphthyl-1)-methyl ester. To the magnesium-organic compound prepared from 27.3 g of α-bromo-β-methoxynaphthalene, dissolved in a 4-fold quantity of anhydrous ether, ethyl formate (3.7 g) dissolved in twice its quantity of ether was added. The mixture was heated for 3 hours, and then diethyl oxalate (14.6 g) was added to it, and the mixture was heated for 3 hours, and then diethyl oxalate (14.6 g) was added to it, and the mixture was heated for 3 hours more. After decomposition of the reaction mixture and separation of the water-insoluble magnesium oxalate, the ether layer was washed with water. The di-(2-methoxynaphthyl-1)-methyl ether, which was difficultly soluble in hydrous ether was purified by recrystallization from methyl alcohol. Its m.p. was 265-266°. The yield was 40%.

0.0846 g subst.: 0.2545 g CO_2; 0.0423 g H_2O. 0.0622 g subst.: 3.45 ml 0.1 N $AgNO_3$. Found %: C 82.09; H 5.60; OCH_3 18.70. $C_{43}H_{38}O_5$. Calculated %: C 82.36 H 5.71; OCH_3 18.50.

SUMMARY

1. The reactions of the magnesium halide-alcoholates of the primary aromatic alcohols, secondary alkylarylcarbinols and tertiary-dialkylarylcarbinols with esters were studied. It was found that the magnesium halide-alcoholates of benzyl alcohol, with equimolecular quantities of esters, form benzyl halides and benzyl esters. Similar to the alcoholates of the

* Together with L. V. Ushakova, M. N. Rybakova, V. F. Maksimov, T. N. Lobanova, N. E. Evstafyeva, N. F. Panaska and V. E. Tarasova.

secondary aliphatic-aromatic alcohols, the halides and unsaturated hydrocarbons become almost the sole reaction products of the tertiary-dialkylarylcarbinolates. With diethyl oxalate, the magnesium halide-bornylates form the ethylbornyl and dibornyl esters of oxalic acid.

2. We synthesized and described the previously unknown compounds: phenyl-(2-ethoxynaphthyl-1)-carbinol, di-(2-methoxynaphthyl-1) carbinol, di-(2-ethoxynaphthyl-1)-carbinol and di-(2-methoxynaphthyl-1)-methyl ether.

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* See Consultants Bureau Translation, page 281.

SYNTHESIS OF IODO-DERIVATIVES OF THE FURAN SERIES

5-IODOFURFURALDEHYDE

Z. N. Nazarova

The iodine-substituted furan series cannot be obtained via the diazo compounds by the characteristic method for obtaining aromatic compounds. Only 5-chloro- and 5-bromo-substituted derivatives [1, 2] were obtained by the direct halogenation of furan derivatives.

A series of iodine-substituted furans was obtained via the mercuric chloride derivatives, which were formed either from the salts of 2-furan-carboxylic acid [1, 3], or by the direct mercurization of furan and its derivatives [1, 3, 4].

However, not all of the furan derivatives are mercurized readily and smoothly; the reaction is frequently accompanied by the formation of di-, tri- and tetra-mercuric derivatives [3, 5, 6]. Thus, on mercurization of furfuraldehyde diacetone, Scheibler and others [6] obtained a mixture of substituted mercuric derivatives; on treatment of the latter with iodine, the authors isolated a mixture of iodinated furfuraldehydes, among which was observed a small quantity of mono-iodofurfuraldehyde, with a m.p. of 110°. However, its structure was not established. By iodination of monochloromercuro-furfuraldehyde [4], synthesized from furfuryl alcohol by the ester method, iodofurfuraldehyde with a m.p. of 127.5° was obtained in a yield of 46%, which on conversion to the alcohol amounted to a total of 4.5%. The structure of the iodofurfuraldehyde thus obtained was demonstrated by its conversion, by the Cannizzaro reaction in the presence of traces of hydrogen peroxide, to 5-iodofuran-2-carboxylic acid.*

Until the present time, iodofurfuraldehyde was not readily available and was a little-studied compound. The development of a method for its production revealed a method of synthesis of new preparations which are of great interest physiologically.

Considering the relative ease of substituting a halide for a nitro-group in the 5-position of the furan nucleus [8], it was of interest to investigate the feasibility of obtaining an iodine-substituted furan series by the exchange reaction of bromine by iodine, by means of alkali metal halides in organic solvents [9].

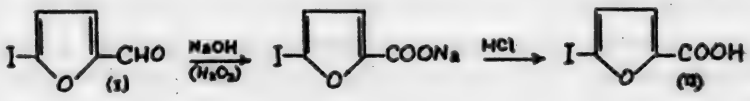
The results which we obtained showed that this reaction can be used successfully for the production of the 5-iodosubstituted derivative of furan. Thus, we were able to obtain a yield of more than 90% of iodofurfuraldehyde (I) by heating 5-bromofurfuraldehyde with an alkali metal iodide in a solution of glacial acetic acid.

Earlier [2] we showed the feasibility of obtaining a 60% yield of bromofurfuraldehyde by the direct bromination of furfuraldehyde. Thus, by this method, iodofurfuraldehyde can be obtained via bromofurfuraldehyde, in a yield of 54% on conversion to furfuraldehyde.

The 5-iodofurfuraldehyde consisted of stable yellowish needles (from dioxane or alcohol), which had a m.p. of 127.5-128°; they decomposed at the boiling point (about 227°), and were practically insoluble in water, highly soluble in dioxane, and more difficultly soluble in alcohol; they were steam-distilled; iodine was liberated quantitatively on heating the crystals with nitric acid.

5-Iodofurfuraldehyde readily formed an oxime which consisted of yellowish needles with a m.p. of 167-168° (decomposed); it gave a semicarbazone which consisted of small yellow needles, which decomposed at 197-199° without melting.

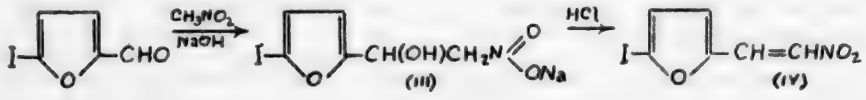
Upon treatment of iodofurfuraldehyde with a 30% aqueous solution of sodium hydroxide, in the presence of traces of hydrogen peroxide, we also obtained a 58% yield of 5-iodofuran-2-carboxylic acid (II) [4], with a m.p. of 192°.



* The 5 iodofuran-2-carboxylic acid was synthesized from 2,5-diiodofuran [7].

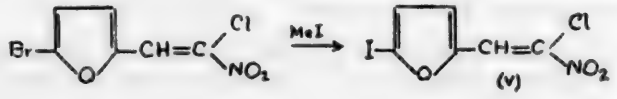
Like bromofurfuraldehyde [10], iodofurfuraldehyde readily undergoes the Perkin reaction, with the formation of an 82% yield of 5-iodofurylacrylic acid. The 5-iodofurylacrylic acid consisted of lustrous, yellow flakes with a decomposition point of 159-160°; they were insoluble in the cold in water and poorly soluble in boiling water; they were highly soluble in dioxane, but more difficultly soluble in alcohol. Iodine was liberated quantitatively by the action of nitric acid.

The iodofurfuraldehyde also condensed with nitromethane, forming an 86% yield of 5-iodofurylnitroethylene (IV). The reaction took place with the formation of the sodium salt of the corresponding nitro-alcohol (III). The latter could be separated from the anhydrous salt as an unstable oil, by cautious acidification with acetic acid; by the action of mineral acids and also by steam distillation, it was converted to iodofurylnitroethylene (IV), which consisted of orange-red flakes with a m.p. of 112-113° (from alcohol).



Iodofurylnitroethylene has an irritating action, and dissolves easily in organic solvents, but is insoluble in water. We also obtained 5-iodofurylnitroethylene, in an 82% yield, from 5-bromofurylnitroethylene [8] by the exchange reaction of bromine by iodine with alkali metal iodide in a solution of acetic acid.

5-Bromofuryl-ω-chloronitroethylene [8] also enters into an exchange reaction with alkali metal iodide. In this case, the exchange of halide proceeds only in the furan nucleus, with the formation of 5-iodofurylchloronitroethylene (V):



The chlorine in 5-nitrofuryl-ω-chloronitroethylene [8] $\left(O_2N-C_4H_2O-CH=C<^{Cl}_{NO_2}\right)$, does not enter into the exchange reaction.

The iodofurylchloronitroethylene consisted of orange-cinnamon leaflets with a m.p. of 109-109.5° (from alcohol); they possessed an irritating action.

Both 5-iodofurylnitroethylene and 5-iodofurylchloronitroethylene, on heating with nitric acid, liberated iodine quantitatively, but unlike the corresponding 5-bromo-substituted derivative [8], the formation of 5-nitrosubstituted derivative was not observed.

EXPERIMENTAL

The ease with which the 5-iodo- and 5-bromo-substituted derivatives of furan liberated halide on heating with nitric acid induced us to attempt to determine the halogen quantitatively. A weighed portion (0.05-0.15 g) of the substance was placed in a conical flask (200 ml capacity) with a ground-glass stopper, and approximately twice the quantity of $AgNO_3$ required theoretically and 5-6 ml of HNO_3 (d 1.4) were added. The flask was left in a dark place for 48 hours, with periodic shaking, after which it was placed in a tepid bath (50-60°) until nitrogen oxides appeared. As usual, a further check was made by determination of the halogen gravimetrically.

We verified the present method for seven 5-halogen-substituted derivatives of furan. Also, parallel halogen analyses of these compounds were made by the Carius method. The results of these analyses are cited in the Table.

The data obtained showed that the ease of displacement of halide by nitric acid in the 5-substituted derivatives of furan may be utilized not only as a qualitative reaction for halide in these compounds, but also for their quantitative determination.

5-Iodofurfuraldehyde

A mixture of 35 g (0.2 mole) of bromofurfuraldehyde [2], 35 g (0.21 mole) of anhydrous KI, and 180 ml of glacial acetic acid was boiled under reflux for 1 hour; on cooling, the mixture was poured, with stirring, into 1 liter of water. After 2 hours the precipitate which came down was separated, washed with water and dried. The yield was 37.1 g (96%); the m.p. was 124-126°. The crude product was dissolved in 30 ml of hot alcohol, and boiled with activated carbon for 15 minutes. After addition of an equal volume of hot water to the filtrate, the iodofurfuraldehyde quickly crystallized as small, yellowish needles. 30.8 g (80%) of iodofurfuraldehyde with a m.p. of 126-127° was obtained. After a second recrystallization from alcohol (or dioxane), and careful drying in a vacuum-desiccator, the almost colorless needles had a m.p. of 127.5-128°. They did not change under storage, and were stable toward the action of dilute solutions of alkali. Iodine vapor, liberated by heating with HNO_3 (d 1.35), crystallized on the walls of the vessel.

Found %: I 57.24. $C_5H_3O_2I$. Calculated %: I 57.19.

TABLE

Results of the Determination of Halogen in 5-Bromo- and 5-Iodo-substituted Derivatives of Furan

Test No.	Substance analyzed	Empirical formula	Melting point	Halide, calculated (%)	Halide, found according to Carius (%)	According to our method		
						weighed portion of substance (g)	total AgX (g) where X = Br or I	halide found (%)
1	Bromofurfuraldehyde	$C_5H_3O_2Br$	82-83°	45.68	45.46	0.1234	0.1334	45.98
2	Iodofurfuraldehyde.	$C_5H_3O_2I$	127.5-128	57.19	57.24	1.1590	0.1684	57.25
3	Bromofurylnitroethylene. . . .	$C_6H_4O_3NBr$	117-118	36.67	36.82	0.1198	0.1021	36.26
4	Iodofurylnitroethylene.	$C_6H_4O_3NI$	112-113	47.91	47.87	0.0482	0.0425	47.66
5	Iodofurylnitroethylene.	$C_6H_4O_3NI$	113-113.5	47.91	47.59	0.1258	0.1102	47.34
6	Bromofurylchloronitroethylene	$C_6H_2O_3NClBr$	74-75	31.66 (Br) 45.71 (Cl+Br)	45 47	0.1375	0.1036	32.05
7	Iodofurylchloronitroethylene	$C_6H_2O_3NClI$	109-109.5	42.38 (I) 54.23 (Cl+I)	54.34	0.1024	0.0802	42.33
8	Iodofurylacrylic acid	$C_7H_5O_3I$	159-160	48.09	47.90	0.1168	0.1023	47.34

The oxime of 5-iodofurfuraldehyde. To a solution of 7 g of hydroxylamine hydrochloride and 3.5 g of anhydrous sodium carbonate in a minimum quantity of water, we added, with shaking, a solution of 7 g of iodofurfuraldehyde in 50 ml of alcohol, and allowed the mixture to stand for 2 days. Gradually, large yellowish flakes crystallized. After recrystallization from 60% alcohol, they were small, almost colorless needles with a m.p. of 167-168° (decomposition). By settling with water, we obtained a still further quantity of the oxime from the mother liquor. The total yield was 5.7 g (76.3%).

0.1034 g sub.: 0.1026 g AgI. Found %: I 53.62. $C_5H_4O_2NI$. Calculated %: I 53.57.

The oxime was soluble in alcohol and poorly soluble in water; iodine was liberated at room temperature by nitric acid. The oxime did not have a sweet flavor.

The semicarbazone of 5-iodofurfuraldehyde. On mixture of hot solutions of 5 g of semicarbazide hydrochloride and 4.2 g of sodium acetate in 4 ml of water, and 4 g of iodofurfuraldehyde in 25 ml of alcohol, small yellow, lustrous needles of the semicarbazone precipitated immediately. The yield was 4.8 g (95.4%). After recrystallization from alcohol, the decomposition point was 199-200°. Iodine was liberated by nitric acid.

0.0810 g sub.: 0.0678 g AgI. Found %: I 45.24. $C_6H_6O_2N_3I$. Calculated %: I 45.50.

5-Iodofurancarboxylic Acid [4]

A mixture of 2.22 g of iodofurfuraldehyde, 55.5 ml of a 30% aqueous solution of sodium hydroxide, and 3 drops of hydrogen peroxide was allowed to stand for 4 days with periodical shaking; water was later added until the sodium iodofurancarboxylate precipitate dissolved, and the solution was treated twice with ether. The alkaline solution was made acidic to Congo with concentrated hydrochloric acid; thus, the almost colorless precipitate of iodofurancarboxylic acid came down instantly. After several hours, the precipitate was filtered off, washed with cold water and dried

over calcium chloride in a vacuum-desiccator. The yield was 1.4 g (58.8%). After recrystallization from hot water, its m.p. was 192°; from benzene the m.p. was 197-198° (decomposed). Iodine was liberated by heating the iodofuran-carboxylic acid with nitric acid.

0.0525 g sub.: 2.2 ml 0.1 N KOH. Found: equiv. 238.5. $C_5H_3O_3I$. Calculated: equiv. 237.9

5-Iodofurylacrylic Acid

A mixture of 13.3 g (0.06 mole) of iodofurfuraldehyde, 25.5 g (0.25 mole) of acetic anhydride, and 6 g (0.061 mole) of three-times remelted potassium acetate was heated, with stirring, under an air condenser, on an oil bath at a bath temperature of 145-150°. After addition of 50 ml of water, the reaction mixture was boiled for 15 minutes longer, then the hot solution was carefully decanted from the resinous deposit, and the residue was repeatedly extracted with hot water. The aqueous solution was made acidic to Congo with hydrochloric acid. The iodofurylacrylic acid quickly crystallized as lustrous, yellow flakes. The yield was 13 g (82.2%). The crude product was purified by boiling its dioxane solution with activated carbon, and precipitating it from the filtrate with hot water. The yellow flakelets obtained decomposed at 159-160° with the evolution of free iodine.

0.0958 g sub.: 0.0849 g AgI. 0.1000 g sub.: 3.8 ml 0.1 N KOH. Found %: I 47.90; equiv. 263.1. $C_7H_5O_3I$. Calculated %: I 48.09; equiv. 263.9.

5-Iodofurylnitroethylene

a) The condensation of 5-iodofurfuraldehyde (0.01 mole) with nitromethane (0.01 mole) was carried out under the conditions described for bromofurfuraldehyde [8]. A yellow-orange precipitate of iodofurylnitroethylene was obtained. The yield was 86%. After 2 recrystallizations from alcohol the orange-red flakes had a m.p. of 112-113°; they were highly soluble in dioxane and acetone, but were more difficultly soluble in alcohol, and were insoluble in water.

0.0945 g sub.: 0.0837 g AgI. Found %: I 47.87. $C_6H_4O_3NI$. Calculated %: I 47.91.

The condensation was carried out in a similar way, except that the reaction mass was not diluted with water and was not decomposed with acid, but the precipitate of the sodium salt (2.74 g, 90%) which formed was separated, washed with cold methanol and anhydrous ether, dried in a vacuum-desiccator, and carefully decomposed with acetic acid until its reaction was slightly acidic (to litmus). The mixture was extracted with ether, and the ether extract was washed with a 1% solution of sodium bicarbonate. After removal of the ether in a vacuum-desiccator, we obtained an orange-red oil, which on storage gradually yielded orange-red crystals. The oil was steam-distilled; yellow-orange crystals were obtained. The yield was 80%. The m.p. was 99-100°. The orange-red plates from alcohol had a m.p. of 112-113°.

b) Exchange reaction of 5-bromofurylnitroethylene [8] with MeI. A mixture of 1 g of bromofurylnitroethylene, 2 g of anhydrous KI (or NaI) and 15 ml of glacial acetic acid was heated for 2 hours on the water bath. On cooling, it was poured into 50 ml of water; a dark precipitate came down immediately. The yield was 1 g (82.6%). After 2 recrystallizations from alcohol (with the use of activated carbon), the orange-red plates had a m.p. of 113-113.5°. A sample of a mixture with known 5-iodofurylnitroethylene gave no m.p. depression. Iodine was liberated on heating with nitric acid; nitrofurylnitroethylene was not observed.

Found %: I 47.35. $C_6H_4O_3NI$. Calculated %: I 47.91.

5-Iodofurylchloronitroethylene

A mixture of 0.7 g of 5-bromofurylchloronitroethylene [8] (m.p. 74-75°), 1 g of NaI and 7 ml of glacial acetic acid was heated for 2 hours on the water bath, and on cooling was poured into 50 ml of water. A dark precipitate came down. The yield was 0.4 g (48.2%). After recrystallization from alcohol, the orange-cinnamon leaflets had a m.p. of 109-109.5°. They had an irritating action. Iodine was liberated by heating the crystals with nitric acid.

0.0409 g sub.: 0.0518 g (AgCl + AgI). Found %: (Cl + I) 53.34. $C_6H_3O_3NClI$. Calculated %: (Cl + I) 54.23.

SUMMARY

1. We showed the feasibility of production of iodofurfuraldehyde and ω-nitrovinylated 5-iodo-substituted furan by exchange reactions of the corresponding bromo-substituted derivatives with alkali metal iodides.

2. Iodofuraldehyde, which was obtained in a 90% yield, and its derivatives, the oxime and the semicarbazone, which had not been described in the literature, were characterized.

3. For the first time, the condensation of iodofurfuraldehyde with nitromethane, and the Perkin reaction, were carried out. We obtained 86 and 82% yields, respectively, of 5-iodofurylnitroethylene and 5-iodofurylacrylic acid, which had not been described in the literature.

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** See Consultants Bureau Translation, page 97.

THE COMPLETE SYNTHESIS OF PSEUDOIONONE

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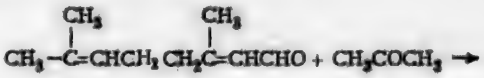
Pseudoionone (VIII) is a substance that poseses great significance for the perfumery industry as an intermediate in the synthesis of α- and β-ionones.

At the present time, the latter compound has also acquired interest as the starting material for the synthesis of vitamin A and carotinoids. Both of the isomeric ionones are obtained by the cyclization ofpseudoionone (VII) in acid medium, in which connection, depending on the character and concentration of the cyclization agent, one of the isomers is obtained in predominant amount.

Pseudoionone (VII) is obtained by the condensation of natural occurring citral (VIII) with acetone under the influence of alkaline agents.



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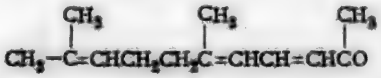
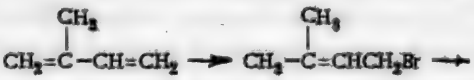


(VII)

The sources of citral (VIII) are the natural ethereal oils or those containing this substance in appreciable quantity (for example, lemon-grass, spike-lavender, etc.), or giving it as the result of the oxidation of linalool (coriander oil). In recent times many papers have been devoted to the problem of the partial synthesis of pseudoionone; however, up to now the complete synthesis of pseudoionone has not been disclosed.

The complete synthesis of pseudoionone developed by us is described in the present paper [1].



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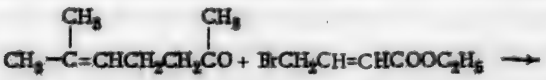

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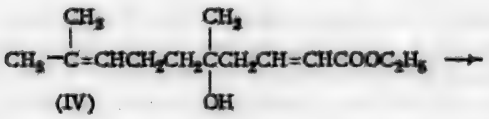

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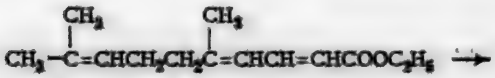

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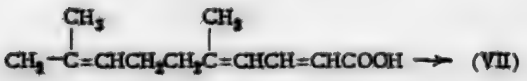


(VI)

The first stage in the given synthesis is the known [2] preparation of 2-methyl-2-hepten-6-one or methylheptenone (II) proceeding from isoprene [3] through γ,γ-dimethylallyl bromide (I), which is further condensed with acetoacetic ester.

In this synthesis Arens and van Dorp [2] saponified the alkylated acetoacetic ester by shaking it with an aqueous alcohol solution of sodium hydroxide, followed by extraction of the unsaponified portion from the alkaline solution with ether. Inasmuch as partial decarboxylation also took place under these conditions with the formation of methylheptenone, there was considerable loss of this product due to its removal along with the unsaponified material. We found it possible to avoid this loss if, after the saponification with alcoholic alkali, the solution was made acid and the methylheptenone was removed by steam distillation. The yield of distilled product was about 60%. The methylheptenone (II) obtained in this manner was condensed (in benzene in the presence of zinc amalgam) with the ethyl ester of γ-bromocrotonic acid (III) to give the ethyl ester of 5,9-dimethyl-2,8-dien-5-hydroxydecanoic acid (IV). The latter was dehydrated with phosphorus oxychloride in the presence of pyridine to the ethyl ester of 5,9-dimethyl-2,4,8-trienedecanoic acid (V). The free acid (VI) obtained after saponification of the ester was converted into pseudoionone (VII) by treatment with methyllithium.

The starting ethyl ester of crotonic acid was obtained by the hydrogenation of acetoacetic ester with skeletal nickel catalyst at 100-150° and an initial pressure of 100-130 atm.

The β-hydroxybutyric ester was dehydrated by the method of distilling its acetyl derivative in the presence of potassium acetate. When the obtained ester is saponified the trans-crotonic acid is readily obtained in crystalline form, which indicates the formation of the trans-configuration when the double bond is created by the method of splitting off the elements of acetic acid.

The ethyl ester of crotonic acid was brominated with N-bromosuccimide in the presence of benzoyl peroxide [4].

The condensation of methylheptenone with the ethyl ester of γ-bromocrotonic acid was effected with the aid of zinc, which had been activated by treatment with concentrated sulfuric acid (with traces of nitric acid) and then amalgamated; here, as in all of the other cases described by us, the amalgamation of the zinc not only accelerates the Reformatsky condensation reaction, but it also facilitates the dehydration of the intermediate hydroxy esters. The reaction product fails to dehydrate under the influence of p-toluenesulfonic acid in boiling toluene, but does suffer complete dehydration when treated with phosphorus oxychloride in the presence of pyridine. The ester (V), isolated by the usual methods and purified by distillation in vacuo, was obtained in a yield of 60-65%, based on methylheptenone.

The dehydration of the hydroxy ester, obtained from methylheptenone by its condensation with bromoacetic ester via the Reformatsky reaction [5], is described in the literature. When dehydrated with phosphorus tribromide in the presence of pyridine, or when the acetyl derivatives were subjected to slow distillation, the products obtained were the isomeric compounds.

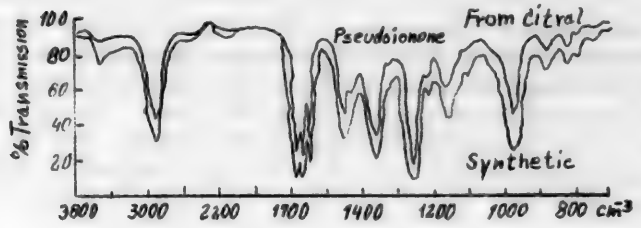
The dehydration of the hydroxy ester (IV) with phosphorus oxychloride in the presence of pyridine gave us the unsaturated ester, possessing a single ultraviolet absorption maximum at 275 mμ, log ε 4.13 and, consequently, containing only one system of two conjugated double bonds, associated with the carboxyl group. Saponification of the ester gave the acid (VI), which with p-bromobenzylisothiuronium bromide was readily converted into the crystalline derivative with m.p. 151-152°.

The addition of an ether solution of two moles of methyllithium [6] to an ether solution of the acid (VI) results in the formation of pseudoionone (VII). The yield of ketone with b.p. 91-92° (0.2 mm) is 80-85%. Psuedoionone also has only one ultraviolet absorption maximum at 290 mμ. Consequently, the presence of a double bond in the part of the molecule formed from the crotonic ester residue determines the position of the second multiple bond, arising in the dehydration of the hydroxy compound.

An examination of the infra-red transmission spectrum of the synthetic psuedoionone and its comparison with the spectrum of the compound obtained by the condensation of citral with acetone reveals a complete coincidence of all of the characteristic bands [7]. In our first communication [1] it was noted that a certain difference existed in the two spectra, which, apparently, was due to traces of impurities.

The band of the carbonyl group at 1675 cm^{-1} is displaced toward the longer wave lengths under the influence of being associated with the system of unsaturated bonds. The presence of the diene grouping is noted by an absorption band at 1590 cm^{-1}, while the third band in this region (1635 cm^{-1}) characterizes the grouping $C=C(CH_3)_2$. The spectrum fails to show any indications of the presence of stereoisomers at the double bonds.

By the cyclization of synthetic psuedoionone with concentrated sulfuric acid under known conditions we were able to obtain β-ionone, which was characterized by the analysis of its crystalline semicarbazone.



EXPERIMENTAL

γ,γ-Dimethylallyl Bromide (I)

Isoprene (50 g) was mixed with 20 ml of 37% hydrobromic acid solution in glacial acetic acid with ice cooling. After standing for two days in the cold, the solution was poured into 1 liter of ice water. The dark oil was separated, dried over calcium chloride, and distilled in vacuo. Colorless liquid with b.p. 52-53.5° at 60 mm. Yield of γ,γ-dimethylallyl bromide, 80 g (73%).

2-Methyl-2-hepten-6-one (Methylheptenone) (II)

Into a flask, fitted with stirrer, reflux condenser and dropping funnel, was charged 200 ml of anhydrous ethyl alcohol, 9.2 g of metallic sodium was introduced in portions, and after cooling there was added 52 g of acetoacetic ester. The reaction mass was heated up to the boil and with stirring there was gradually added 60 g of γ,γ-dimethylallyl bromide over a period of 30-40 minutes. A precipitate of sodium bromide was obtained in measure with the addition. The mixture was cooled, filtered, 120 ml of alcohol was distilled off in vacuo, 250 ml of 2 N sodium hydroxide solution was added and the mixture stirred at 50-60° for 2 hours, then dilute sulfuric acid was added to acid reaction, and the mixture was steam distilled. The upper layer was separated, the aqueous layer was extracted with ether, the combined extracts washed with saturated sodium bicarbonate solution, and then dried over sodium sulfate. After removal of the ether, the residue was distilled in vacuo. Yield 29.5 g (58%).

B.p. 61-62° (12 mm), n_D^{20} 1.4408.

Ethyl γ-Bromocrotonate (III)

a) Ethyl β-hydroxybutyrate. Into a rotated autoclave, electrically heated and having a capacity of 1 liter, was charged 260 g of freshly distilled acetoacetic ester, 14 g of skeletal nickel catalyst, and sufficient hydrogen to give a pressure of 100-120 atm. The hydrogenation was run at 100-150° for 1-1.5 hours. After cooling, the catalyst was filtered and the filtrate was distilled in vacuo. B.p. 67-68° (4 mm). Yield of hydroxybutyrate, 220 g (84%).

b) Ethyl crotonate. The β-hydroxybutyric ester (132 g), with ice-water cooling, was mixed with 112 g of acetic anhydride and 1 ml of sulfuric acid, the acetic acid formed in the reaction was removed by distillation in vacuo. 22 g of anhydrous potassium acetate was added to the residue, and the mixture distilled at atmospheric pressure. The obtained ester was washed with saturated sodium bicarbonate solution, dried over calcium chloride, and the crotonic ester distilled. Yield 78-80 g (68.5-70%), on acetoacetic ester 55-61%.

B.p. 136-140°, n_D^{20} 1.4252.

c) Crotonic acid. A mixture of 6 g of the crotonic ester and 60 ml of 10% potassium hydroxide solution was heated on boiling water until the oil layer disappeared (40-45 minutes). After cooling, the unsaponified portion was extracted with ether, most of the water was distilled off in vacuo, the residue was acidified with 10% sulfuric acid, and the crotonic acid was extracted with ether. The ether extract was dried over sodium sulfate. After distilling off the ether, the crotonic acid is obtained with m.p. 70-71°. Yield 3.8-4.0 g (85-90%).

d) Bromination of the crotonic ester. The ethyl crotonate (114 g) was dissolved in 500 ml of dry benzene, and then 100 g of bromosuccimide and 100 mg of freshly precipitated dibenzoyl peroxide were added. The heating was continued until a negative reaction for bromine was obtained with starch iodide paper. The mixture was cooled, the deposited succimide was removed by filtration, the filtrate washed with a saturated aqueous solution of sodium bicarbonate, and then dried over sodium sulfate. After distilling off the benzene, the residue was distilled in vacuo

at 10 mm to give two fractions: 1st fraction 60-65°, 22-25 g, crotonic ester; 2nd fraction 111-113°, 85-90 g, bromocrotonic ester. Yield, 56-59%.

The recovered ethyl crotonate was used in subsequent bromination experiments.

Ethyl Ester of 5,9-Dimethyl-2,8-dien-5-ol-decanoic Acid (IV)

Methylheptenone (12.6 g) (0.1 mole) and 25.8 g (0.13 mole) of ethyl γ-bromocrotonate were dissolved in 140 ml of anhydrous benzene and the obtained solution was gradually added with stirring to 13 g of activated zinc catalyst, covered with dry boiling benzene. The reaction began after several minutes, and the boiling continued due to the evolution of heat. After all of the solution had been added, the mixture was heated for another 40-45 minutes, then it was cooled and 50 ml of 10% acetic acid solution was added. The benzene layer was separated, washed with a saturated aqueous solution of sodium bicarbonate, and dried over sodium sulfate. From the obtained benzene solution the benzene was distilled off in vacuo down to a volume of 50 ml. The evaporated solution was used for the dehydration reaction.

Ethyl Ester of 5,9-Dimethyl-2,4,8-trienedecanoic Acid (V)

To a mixture, heated to the boil, of 50 ml of benzene, 50 ml of pyridine and 10 ml of phosphorus oxychloride was added from a dropping funnel with stirring 50 ml of a benzene solution of the hydroxy ester. Heating was continued for 45 minutes after completion of addition, the mixture was cooled, poured on ice, the benzene layer separated, washed with dilute sulfuric acid and water, and dried over sodium sulfate. After removal of the benzene, the residue was distilled in vacuo. Yield of ester (V) 14.2 g (63-64% on methylheptenone). The Tserevitinov reaction for active hydrogen was negative.

B.p. 90-92° (0.2 mm), 102-104° (4 mm), d_D 0.93397, n_D^{20} 1.4952.

Found %: C 75.47; H 10.25. MR_D 67.9. $C_{14}H_{22}O_2$. Calculated %: C 75.65; H 9.91. MR_D 67.105. $E_{1\,cm}^{1\%}$ 518 for λ_{max} 275 mμ.

5,9-Dimethyl-2,4,8-trienedecanoic Acid (VI)

A mixture of 13.8 g of the ester (V) with 50 ml of 10% alcoholic potassium hydroxide solution was heated on the water bath for 2 hours. The mixture was poured into water, the unsaponified portion extracted with ether, the water layer acidified with 10% sulfuric acid solution, extracted with ether, and the ether extract dried over sodium sulfate. The solvent was removed to give the free acid as a mobile, yellow oil. Yield, 9.7-10.2 g (81-85%).

Bromobenzylisothiuronium salt of 5,9-dimethyl-2,4,8-trienedecanoic acid. To a solution of 0.6 g of the acid (VI) in 5 ml of 3.75% aqueous KOH solution with heating was added a hot solution of 1 g of p-bromobenzylisothiuronium bromide in 5 ml of ethanol. The salt precipitated immediately as a white deposit. After three recrystallizations from ethyl alcohol, m.p. 151.5-152°.

Found %: N 6.52. $C_{28}H_{37}O_2SN_2Br$. Calculated %: N 6.38.

Psuedoionone (VII)

To a solution of 9.2 g of the acid (VI) in 100 ml of dry ether with stirring was added 300 ml of an ether solution of methyllithium (containing 3.2 g of methyllithium). After all of the methyllithium had been added, the reaction mixture was stirred for another 30-40 minutes, then poured into water, the ether layer separated, and the aqueous layer extracted with ether. The combined ether extracts were dried over sodium sulfate. The psuedoionone was obtained as a light yellow oil with characteristic odor.

B.p. 91-92° (0.2 mm), n_D^{20} 1.5262, log ε 4.4 at λ_{max} 290 mμ.

Found %: C 81.05; H 10.36. $C_{13}H_{22}O$. Calculated %: 81.25; H 10.41.

β-Ionone (Cyclization of Synthetic Psuedoionone)

A solution of 5 g of synthetic psuedoionone in 20 ml of dry ether was added with stirring and cooling from −10° to −20° to 20 ml of concentrated sulfuric acid. The reaction mixture was poured over ice, the ether layer separated, the aqueous layer extracted with ether, the ether extracts washed with a saturated aqueous solution of sodium bicarbonate, and then dried over sodium sulfate. The ether was removed and the residue was distilled in vacuo. β-Ionone was obtained as a light yellow oil with b.p. 72-74° (0.1 mm). Yield, 3.2 g (64%).

The semicarbazone of β-ionone was obtained in the usual manner. After two recrystallizations from anhydrous alcohol, m.p. 146-147°. Melting point of the β-ionone semicarbazone from citral 148-149°. The mixed m.p. was 147-148°.

2.130 mg sub.: 0.323 ml N_2 (22°, 738 mm). Found %: N 17.04. $C_{14}H_{23}ON_3$. Calculated %: N 16.85.

SUMMARY

1. The complete synthesis of psuedoionone was realized, starting from synthetic methylheptenone. The psuedoionone obtained in this manner was identified by its ultraviolet and infra-red absorption spectra and by conversion into β-ionone.

2. In the course of the work, the following compounds were obtained and characterized for the first time: the ethyl ester of 5,9-dimethyl-2,4,8-trienedecanoic acid and 5,9-dimethyl-2,4,8-trienedecanoic acid.

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STUDY OF THE CONDITIONS FOR THE FORMYLATION OF ACYLAMINO ACIDS

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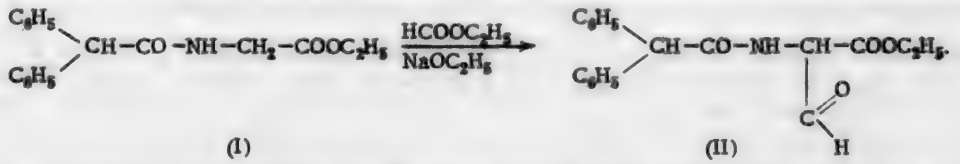
The formylation of N-acylated glycine esters with ethyl formate in the presence of sodium ethylate is one of the convenient methods for the synthesis of penaldic acids and acquires great interest at the present time in connection with the problem of synthesizing penicillin. However, despite the seeming simplicity of this reaction, much labor was required in order to establish the conditions, permitting the undeniable procurement of the desired C-formyl derivative, and to study the other directions in which this reaction can proceed.

This reaction was first used by Erlenmeyer, Jr. [1] in 1904 for the synthesis of ethyl α-formylhippurate. Erlenmeyer was unable to isolate this substance in crystalline form; it was obtained as an oil, being a mixture of the keto and enol forms. The crystalline keto form of the formylhippurate was obtained by A. S. Elina and O. Yu. Magidson [2] with a m.p. of 57-58°. Erlenmeyer, as well as Elina and Magidson [3], indicate that they had run numerous formylation experiments before they were successful in obtaining good yields of the desired products. In addition, it should be mentioned that even strict adherence to the reaction conditions recommended by Erlenmeyer fails at times to give the desired results; instead of the formylhippuric ester the free hippuric acid is obtained.

The reaction conditions used for the condensation process, the solvent, temperature, contact time, condensation agent (Na, sodium ethylate), the method used for decomposing the sodium derivative, all of these strongly influence the direction in which the reaction proceeds. Elina and Magidson [3] developed the optimum reaction conditions for the formation of the α-formylphenaceturic ester, but in this case the yield of desired compound was only 45.4%, for, in addition to the condensation reaction, the ester of phenylacetic acid was formed due to the cleavage of the phenaceturic ester molecule and esterification of the resulting acid. They obtained the ester of phenylacetic acid in a yield of about 30%.

We used the conditions of Elina and Magidson for the synthesis of the ester of α-formyldiphenaceturic acid. This ester was obtained by us as an oil, being a mixture of the keto and enol forms. In addition to the oil, the original diphenaceturic ester was recovered. The yield of formyl derivative was 53%, based on the phenaceturic ester taken for reaction, and 93%, based on the reacted ester. Cleavage of the diphenaceturic ester molecule failed to occur.

The ester of α-formyldiphenaceturic acid (II) is the ester of the penaldic acid, having one phenyl group more than the ester of the penaldic acid from penicillin G.

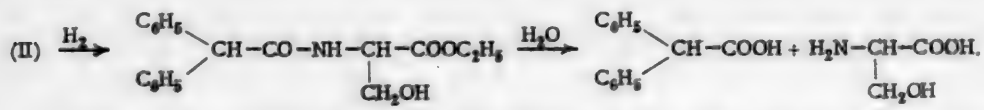


(I) (II)

The diphenaceturic ester (I) needed for the synthesis of the above compound was obtained by us by the condensation of glycine ester hydrochloride with the acid chloride of diphenylacetic acid via a slight modification of the Franzen method [4]; the diphenylacetyl chloride was obtained by heating diphenylacetic acid with thionyl chloride via the Staudinger method [5]. The ester (II) readily gave the 2,4-dinitrophenylhydrazone with m.p. 188-189° and the semicarbazone with m.p. 133-134°. When treated with $FeCl_3$ solution, the ester (II) gives an intense coloration which indicates the presence of an enol grouping in the oil.

In addition to the above, the structure of the ester (II) was demonstrated by the method developed by Erlenmeyer [1] and used by Elina and Magidson [3]; the formyl group of the ester was reduced with aluminum amalgam to the primary alcohol group. The thus obtained ester of N-diphenacetylserine was subjected to hydrolytic cleavage by boiling with dilute (1:15) sulfuric acid. Under these conditions the ester of benzoylserine is completely decomposed into benzoic acid and serine, while the ester of N-phenacetylserine is decomposed into serine and phenylacetic acid. In our case, it proved necessary to use somewhat more drastic conditions, for on heating with H_2SO_4 (1:15) for 8 hours, the ester failed to undergo cleavage. After heating with H_2SO_4 (1:10) for 4 hours, the diphenylacetic

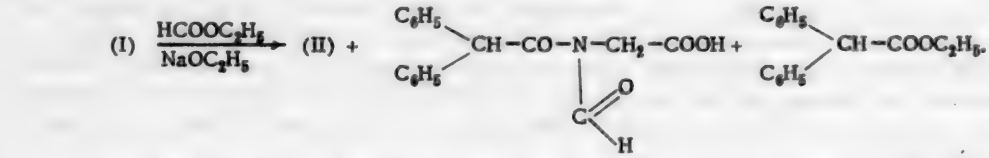
acid was isolated in quantitative yield, but we were unable to isolate the serine, since it resinified under these conditions.



Different conditions can be used for the condensation of esters in the presence of sodium alcoholate; thus, for example, Rabe with coworkers [6, 7] ran the condensation by heating the mixture of esters with dry sodium ethylate in the absence of solvent at 80°. We modified this method somewhat and ran the condensation of the diphenaceturic and formic esters in the presence of sodium alcoholate in anhydrous alcohol medium with heating up to 60-80°. In this case, the reaction proceeded in three directions: an oily substance was obtained, identical with the above described α-formyldiphenaceturic ester, and a crystalline substance with m.p. 156-157°, proving to be N-formyldiphenaceturic acid. Yield, 30%.

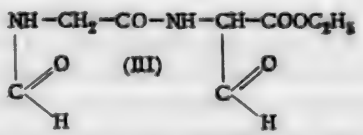
This substance fails to give a coloration with $FeCl_3$ solution, fails to form carbonyl derivatives, fails to give a silver mirror when treated with an ammoniacal silver oxide solution, is not reduced by aluminum amalgam to yield serine derivatives but it does form a silver salt, the analysis of which corresponds to the indicated formula. In contrast to the penaldic acids, this acid fails to suffer decarboxylation when heated.

The third direction of the reaction is the cleavage of the diphenaceturic ester and esterification of the resulting diphenylacetic acid. Yield, 40%. Still another circumstance should be mentioned; whereas in the cold in ether solution, the C-formyl derivative of the ester is obtained, on heating, the N-formyl derivative of the free acid is obtained.



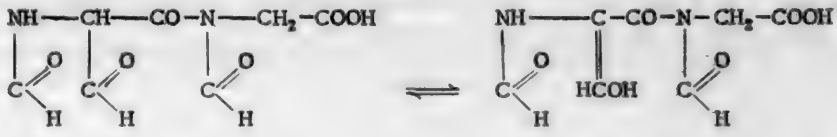
As a result, having shown that depending on the temperature regime for the condensation reaction, it is possible to obtain either the C- or N-formyl derivatives, we decided to verify this on a simpler example – the ester of hippuric acid, and to study this capricious reaction in greater detail. When the condensation reaction was run in the cold, under the conditions of Erlenmeyer and of Elina and Magidson, we obtained an oily substance – a mixture of the enol and keto forms of the α-formylhippuric ester, in a yield of 88.5%. The oil gives an intense coloration with $FeCl_3$ solution, gives a silver mirror with ammoniacal silver oxide solution, the 2,4-dinitrophenylhydrazone (m.p. 178-179°), and the semicarbazone (m.p. 164-165°). Reduction of the oil gave N-benzoylserine (m.p. 80°). We ran the reaction several times under the indicated conditions, but the desired result was not always obtained: one time the original hippuric ester was recovered, another time we obtained hippuric acid.

Having run the reaction with heating up to 60-80° under the above indicated conditions, we calculated on obtaining the N-formylhippuric ester; however, the reaction proceeded in a different manner: from the reaction products we isolated ethyl benzoate, benzoic acid and a crystalline product, the latter as glistening golden-yellow leaflets with m.p. 204-205° (from alcohol). This product gave an acid reaction to litmus and could be titrated with alkali; it gave an intense coloration with $FeCl_3$ solution, and contained the aldehyde group (formation of silver mirror), which, however, failed to give derivatives with 2,4-dinitrophenylhydrazine and semicarbazide; the test for primary amino group was also negative. The presence in the reaction products of ethyl benzoate and benzoic acid, and the high nitrogen content of the obtained crystalline product, made it possible to assume that both N- and C-formylhippuric esters had been formed in the reaction, which esters underwent cleavage with the formation of benzoic acid and the esters of N- and C-formylglycine; the latter condensed with each other under the reaction conditions to yield the ester of N,C-diformylglycylglycine (III):



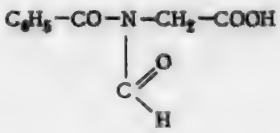
The molecular weight and nitrogen content corresponded exactly to this formula; however, the negative results obtained when we attempted to determine the amount of ethoxyl group caused us to assign to this substance

a different formula with the same molecular weight and nitrogen content, but containing a free carboxyl group – the formula 1,2,4-triformylglycylglycine (IV and IVa):



(IV) (IVa)

The coloration with $FeCl_3$ solution and the formation of a silver mirror indicate the presence of the C-formyl group, in which connection this group cannot exist at the α-carbon atom, since the obtained compound fails to suffer decarboxylation when heated. The aldehyde groups, found at the nitrogen atoms, do not form carbonyl derivatives, as had been seen on the example of N-formyldiphenaceturic acid. In the given case the C-formyl group also failed to react with 2,4-dinitrophenylhydrazine and semicarbazide, possibly because of its being screened by the N-formyl groups. The formula proposed by us cannot be considered as being strictly proved, but it is impossible to assign any other formula, satisfying the chemical properties of the obtained substance and the results of the analytical study. As a result, we were unable to obtain the expected N-formylhippuric acid under the conditions of condensing the hippuric ester with the formic ester in the presence of sodium ethylate and with heating up to 60-80°. We obtained this acid in a different manner: first we obtained the sodium derivative of the hippuric ester by treating this ester with metallic sodium in boiling benzene medium, after which the ethyl formate was added to the reaction mixture. After decomposition of the sodium derivative there was obtained 4 g (20%) of crystalline product, giving an acid reaction to litmus, and failing to give derivatives with 2,4-dinitrophenylhydrazine and semicarbazide. When heated, this product fails to undergo decarboxylation; on the basis of the indicated properties and analytical results it should be assigned the formula of N-formylhippuric acid (V):



(V)

The amount of obtained acid was insufficient for making a more detailed study, but in the numerous attempts made to repeat its preparation we failed to obtain more of the product under the above described conditions: either the molecule suffered cleavage with the formation of ethyl benzoate and benzoic acid and resinification of the second half of the molecule, or hippuric acid was obtained, or the unchanged hippuric ester was recovered. All of these unsuccessful attempts, the same as those described above, demonstrate once more that no matter what conditions are used for the condensation of the hippuric ester with ethyl formate, the condensation proves to be extremely capricious: slight uncontrollable changes in the conditions are sufficient to interfere with the obtaining of reproducible results. Inasmuch as all of the N-formyl derivatives obtained by us had not been obtained earlier by anybody else, and since nothing is said in the literature about the inability of known N-formyl derivatives to form carbonyl derivatives, we decided to synthesize a known N-formyl derivative – N-formylglycine, obtained by Fischer and Warburg [8], and compare its properties with the properties of our compounds. These properties coincided exactly: N-formylglycine fails to give carbonyl derivatives, fails to give a coloration when treated with $FeCl_3$ solution, and fails to form a silver mirror.

EXPERIMENTAL

Glycine ester hydrochloride was obtained by the method of Marvel [9], ethyl formate by the method of Young and Thomas [10], benzoin, benzilic and diphenylacetic acids by the methods described in [11]. The use of phosphorus tri- and pentachlorides in the preparation of diphenylacetyl chloride failed to give good results, while the use of thionyl chloride, according to Staudinger [5], gave the acid chloride in a yield of 90%.

Condensation of glycine ester hydrochloride with diphenylacetyl chloride. To 17 g of diphenylacetyl chloride and 10.5 g of glycine ester hydrochloride, dissolved in 200 ml of dry benzene, was added 10 g of dry soda. The mixture was stirred and heated on the water bath until the evolution of HCl gas had ceased, after which it was allowed to stand overnight. The diphenylaceturic ester precipitates as white, silky needle crystals with m.p. 115-116° (from alcohol). Yield, 16.5 g (78%).

0.0941 g sub.: 3.9 ml N_2 (16°, 747 mm). 0.1521 g sub.: 14.11 g benzene: Δt 0.187°. Found %: N 4.74. M 295. $C_{18}H_{19}O_3N$. Calculated %: N 4.71. M 297.

Preparation of the ethyl ester of α-formyldiphenaceturic acid. To 1.3 g of divided metallic sodium in 40 ml of anhydrous ether was gradually added 4 ml of anhydrous alcohol, and the mixture was boiled until all of the sodium had reacted. After cooling, 5 ml of ethyl formate was gradually added and with stirring (by hand) 15.5 g of the diphenaceturic ester. After standing for 10 days in a tightly stoppered flask the reaction mixture, slightly colored and viscous, was decomposed with ice water and repeatedly extracted with ether. From the ether solution was isolated 7 g of unreacted diphenaceturic ester. The aqueous layer was acidified with dilute sulfuric acid (1:15) and then extracted with ether. After drying over sodium sulfate and distilling off the ether an oily residue was obtained which failed to crystallize, and which proved to be a mixture of the keto and enol forms of the ethyl ester of α-formyldiphenaceturic acid. Yield 9 g. The 2,4-dinitrophenylhydrazone melts at 188-189° (from alcohol).

0.1016 g sub.: 11.9 ml N_2 (18°, 776 mm). Found %: N 13.93. $C_{25}H_{23}O_7N_5$. Calculated %: N 13.86.

Reduction of the ethyl ester of α-formyldiphenaceturic acid. The aluminum amalgam was prepared by the method of Wislicenus and Kauffmann [12], only instead of aluminum turnings we used short pieces of heavy aluminum wire. To 5 g of α-formyldiphenaceturic ester, dissolved in 150 ml of moist ether, was added 15 g of aluminum amalgam, and the vigorous evolution of hydrogen was observed. From time to time several drops of water were added. The reaction was completed after 3 days, which was established by the absence of coloration with $FeCl_3$ solution when a sample from the reaction mixture was tested. The ether solution was filtered from the slime, which was extracted several times with ether. After drying over sodium sulfate and distilling off the ether an oily substance was obtained, which crystallized on standing; yield 2.2 g (44%). The substance is poorly soluble in ether and petroleum ether, and more readily soluble in alcohol and benzene. The ethyl ester of N-diphenylacetylserine crystallizes as colorless needle crystals with m.p. 99-100° (from benzene).

21.18 mg sub.: 0.847 ml N_2 (24°, 763 mm). 0.1042 g sub.: 26.2 g benzene: Δt 0.06°. 0.0398 g sub.: 26.4 ml CH_4 (16° 761.6 mm). Found %: N 4.42; M 333; OH number 0.90. $C_{19}H_{21}O_4N$. Calculated %: N 4.28; M 327; OH number 1.

Cleavage of the ethyl ester of N-diphenacetylserine. When, after boiling 2 g of the ethyl ester of N-diphenacetylserine with 80 g of H_2SO_4 (1:15) for 8 hours, the presence of diphenylacetic acid in the reaction mixture could not be detected, we increased the acid concentration to 1:10. After boiling with this strength of acid for 4 hours, the reaction solution was cooled and the separated diphenylacetic acid was filtered. The filtrate was extracted with ether. The yield of diphenylacetic acid was 1.29 g (90%). For neutralization of the sulfuric acid the calculated amount of $BaCO_3$ was added to the filtrate. After evaporation in vacuo a tarry residue was obtained instead of the serine derivative.

Condensation of the diphenaceturic ester with ethyl formate in anhydrous alcohol in the presence of sodium ethylate with heating to 60-80°. To the sodium ethylate, prepared from 2.8 g of metallic sodium and 30 ml of anhydrous alcohol, was gradually added 11 ml of ethyl formate in which connection noticeable heating up of the reaction mixture was observed. The mixture was allowed to stand for 2 hours, then to it was added 16.3 g of the diphenaceturic ester and the mixture was heated at 60-80° for 2 hours. Gradually, the mixture turned into a thick, dark mass, which was allowed to stand overnight, and then decomposed with ice water; on doing this, the ester of diphenylacetic acid separated out in an amount of 5.2 g (40%), m.p. 57-58° (from alcohol).

Literature data [14]: m.p. 58°.

The saponification of this ester with an alcoholic NaOH solution gave diphenylacetic acid with m.p. 144-145°. The mixed melting point with known diphenylacetic acid failed to show a depression.

The aqueous solution was acidified with dilute sulfuric acid and the separated oil was extracted with ether. After drying over sodium sulfate and distilling off most of the ether the oil began to crystallize. There was obtained 4.8 g (30%) of crystalline product, difficultly soluble in ether, benzene, water and petroleum ether, and readily soluble in alcohol. After several recrystallizations from aqueous alcoho, the product was obtained as white, needle crystals with m.p. 156-157°.

0.0812 g sub.: 2.75 ml NaOH (T 0.0077508). 23.28 mg sub.: 0.995 ml N_2 (18°, 760.8 mm). Found: equiv. 304; % N 4.84. $C_{17}H_{15}O_4N$. Calculated: equiv. 297; % N 4.71.

To a small amount of the acid with m.p. 156-157°, dissolved in alcohol and titrated with alkali, was added a concentrated solution of the calculated amount of $AgNO_3$. The white flocculent silver salt obtained in this manner was filtered, washed with water, and dried in a desiccator.

0.0420 g sub.: 0.0114 g Ag. Found %: Ag 27.01. $C_{17}H_{14}O_4NAg$. Calculated %: Ag 26.66.

Preparation of ethyl hippurate. We obtained this ester by the method of Franzen [4] in a yield of 87%, but a purer product and with a better yield (90%) was obtained by us under the conditions of condensing glycine ester hydrochloride with ethyl chlorocarbonate as described by Fischer and Otto [13].

Condensation of ethyl hippurate with ethyl formate in thepresence of sodium ethylate with heating to 60-80°. To the sodium ethylate, prepared from 4 g of divided sodium and 30 ml of anhydrous alcohol was added 13 ml of ethyl formate; the resulting mixture that had become warm was allowed to stand for 2 hours, then 17.4 g of the hippuric ester was added, and the mixture was heated to boiling for 2 hours. The resulting viscous dark yellow mass was allowed to stand overnight, after which it was decomposed with ice water. The obtained solution was extracted with ether and the extracts were dried over sodium sulfate. After distilling off the ether there was distilled several drops of liquid with b.p. 210-212° (n_D^{20} 1.4987)and possessing the characteristic odor of ethyl benzoate.

Literature data [15]: b.p. 212.9°, n_D^{20} 1.5057.

The acidification of the aqueous solution with dilute sulfuric acid gave a precipitate, which after recrystallization from aqueous alcohol was obtained as glistening yellow scales and melted at 204-205°. Yield 1.3 g. The product is readily soluble in alcohol and dioxane, very poorly soluble in ether and benzene, gives a dark green coloration with $FeCl_3$ solution, gives a positive reaction for nitrogen according to Lassen, forms a silver mirror and shows an acid reaction to litmus; it fails to give a precipitate with 2,4-dinitrophenylhydrazine. From the water alcohol solution obtained after removal of the crystalline product there was isolated benzoic acid by steam distillation, which acid after the distillation had m.p. 120°.

5.88 mg sub.: 0.685 ml N_2 (23°, 760 mm). 0.0902 g sub.: 4.3 ml NaOH (T 0.003875). 0.0567 g sub.: 17.2 g dioxane: Δt 0.075°. Found %: N 12.89; equiv. 216; M 211. $C_7H_8O_2N_2$. Calculated %: N 12.96; equiv. 216; M 216.

Condensation of ethyl hippurate with ethyl formate in the presence of metallic sodium. To a boiling benzene solution of 20 g of ethyl hippurate was gradually added with stirring 2.3 g of metallic sodium in the form of thin ribbon. When all of the sodium had reacted, to the reaction mixture was added 8.7 g of ethyl formate. After several minutes the flask contents turned into a thick brown mass. After standing overnight the obtained product, failing to dissolve in water, was dissolved in alcohol with heating. The acidification of this solution gave a white crystalline precipitate, which was recrystallized from 50% alcohol, m.p. 135-136°. The yield of pure product was 4 g (20%). The obtained product gave an acid reaction to litmus, failed to be decarboxylated when heated, and failed to give derivatives with 2,4-dinitrophenylhydrazine and semicarbazide.

0.1424 g sub.: 9.1 ml N_2 (17°, 734.6 mm). 0.0630 g sub.: 7.10 g benzene: Δt 0.232°. Found %: N 7.12; M 194. $C_{10}H_9O_4N$. Calculated %: N 6.76; M 207.

SUMMARY

1. The condensation of diphenylacetyl chloride with glycine ester hydrochloride gave the diphenaceturic ester.

2. The formylation of the diphenaceturic ester in the presence of sodium ethylate was studied in the cold and with heating.

3. It was shown that when the formylation reaction is run in anhydrous ether in the cold, the α-formyldiphenaceturic ester is obtained in excellent yield.

4. The reduction of the α-formyldiphenaceturic ester gave the ethyl ester of diphenacetylserine.

5. It was shown that on heating the diphenaceturic and formic esters in anhydrous alcohol medium in the presence of sodium alcoholate, in addition to the α-formyldiphenaceturic ester, there are formed the N-formyldiphenaceturic acid and the ethyl ester of diphenylacetic acid.

6. The formylation of ethyl hippurate in the presence of sodium ethylate, and in the presence of metallic sodium, was studied.

7. It was shown that on heating the hippuric and formic esters in anhydrous alcohol medium in the presence of sodium ethylate there is obtained a crystalline product, being, in all probability, 1,2,4-triformylglycylglycine.

8. The condensation of the hippuric and formic esters in boiling benzene in the presence of metallic sodium gave N-formylhippuric acid.

9. On the example of the obtained N-formyl derivatives were studied the properties of the aldehyde group, found at the nitrogen atoms in the molecules of these compounds.

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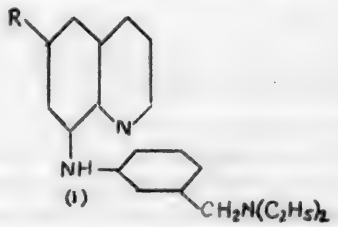
** See Consultants Bureau Translation, page 861.

THE MOBILITY OF THE DIETHYLAMINO GROUP

III. SYNTHESIS OF 8-(AMINOBENZYL)AMINOQUINOLINES

V. I. Stavrovskaya and M. O. Kolosova

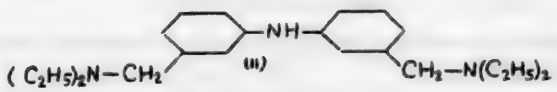
Earlier one of us made a communication on the method used for the preparation of aryl- and quinolyl-8-aminoquinolines [1]. In an attempt to expand this method to certain other arylamines we set outselves the task of obtaining compounds of type (I) (where R = H, OCH_3) for the purpose of elucidating their antimalarial activity.



(I)

For this purpose, we used the same synthesis method, i.e., we heated the mixture of free 8-aminoquinoline or its 6-methoxy derivative with the monohydrochloride of m-aminobenzyldiethylamine in a sealed tube for 18 hours at 170-175°. From the reaction mass were isolated unreacted 6-methoxy-8-aminoquinoline and m-aminobenzyldiethylamine, and also the condensation product, capable of being distilled in vacuo, which was characterized as the picrate. However, the analyses of both the base and of the picrate failed to correspond to the above depicted structure of the substance as being an aryl derivative of 8-aminoquinoline.

In the experiment with 8-aminoquinoline (I, R = H) the melting point of the picrate failed to coincide with the melting point of the picrate from 8-(3'-diethylaminomethylphenyl)aminoquinoline, previously obtained by us by another method [1]. On the assumption that the compound 3,3'-bis-diethylaminomethyldiphenylamine (II) could have been formed in our reaction, we attempted to synthesize it separately by the method of heating a mixture of

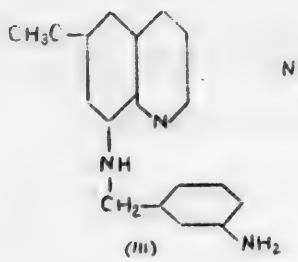


(II)

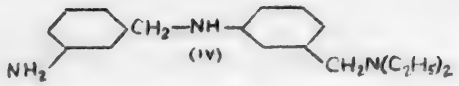
the base with the dihydrochloride of m-aminobenzyldiethylamine in a sealed tube. It should be mentioned that when the liquid base was mixed with the solid dihydrochloride a sticky mass was obtained, which with more assiduous rubbing solidified with unexpected rapidity. The nitrogen analyses for the thus-obtained reaction product also failed to correspond to the structure of 3,3'-bis-diethylaminomethyldiphenylamine. In addition, this substance could be diazotized and coupled with β-naphthol.

It was postulated by us that the reaction between the two amines fails to proceed at the expense of the amino group with the separation of ammonium chloride, but instead that it proceeds with the cleavage of diethylamine hydrochloride at the expense of the amino and diethylamino groups. As a result there should be obtained 6-methoxy-8-(3'-aminobenzyl)aminoquinoline (III) and N-(3'-aminobenzyl)-3-diethylaminomethylaniline (IV).

The nitrogen analyses corresponded to such a structure for the products, also understandable became their ability to be diazotized, and also the strong odor of diethylamine that developed when the product was alkalized after the reaction.



(III)



(IV)

To confirm the above postulation we synthesized N-(3'-aminobenzyl)-3-3diethylaminomethylaniline by another method, namely: from m-nitrobenzyl chloride and m-aminobenzyldiethylamine with subsequent reduction of the nitro group. The obtained base, as well as its hydrochloride, possessed the same properties as the one synthesized earlier. The mixed melting point of the hydrochlorides failed to show a depression.

As a result, the synthesized quinoline derivatives should be assigned the structure of 8-(aminobenzyl)aminoquinolines, instead of the expected 8-phenylaminoquinolines.

It appears to us that such a reaction course is due to the fact that in m-aminobenzyldiethylamine we have two amino groups, differing in their basicity. On mixing the free base of this amine with its dihydrochloride, melting at 222°, there occurs redistribution of the hydrogen chloride and the formation of the monohydrochloride with m.p. 152°. Visually this was manifested in the above indicated hardening of the sticky mixture of the base and hydrochloride of m-aminobenzyldiethylamine. It must be thought that in view of the greater basicity of the diethylamino group, the salt formation proceeds for the most part at its expense.

In the literature are described reactions, proceeding between quaternary salts, containing the benzyl group, and acetoacetic ester [2], amines [3] or Na_2Te [4], KCN, NaSH, Na_2S, etc. [5]. Benzyldiethylamine hydrochloride reacts with a number of aromatic amines [6]. In all cases, there occurs cleavage of the dialkylamine.

It is possible that the easier salt formation properties of the diethylamino group in our case facilitates the direction of the reaction specifically at the expense of cleavage of the diethylamino group. Together with this it is evident that here a role is also played by the greater mobility of the diethylamino group, when compared with the amino group, since in the presence of both groups in the same compound the reaction always proceeds with the cleavage of the diethylamine hydrochloride.

The reaction also takes place if the m-aminobenzyldiethylamine is taken as the dihydrochloride. However, here there was observed a considerable decrease in the yield of 6-methoxy-8-(3'-aminobenzyl)aminoquinoline and the formation of 6-methoxy-8-(6'-methoxy-8'-quinoline)aminoquinoline.

All of the synthesized compounds proved to be inactive when tested for avian malaria.

EXPERIMENTAL

6-Methoxy-8-(3'-aminobenzyl)aminoquinoline

a) An intimately ground mixture of 6-methoxy-8-aminoquinoline (8.7 g), m-aminobenzyldiethylamine free base (4.5 g) and m-aminobenzyldiethylamine dihydrochloride (6.3 g) was heated in a sealed tube for 18 hours at 170-175°. After cooling, the obtained dark brown melt was dissolved in 10% hydrochloric acid and the acid solution was cooled with ice; this resulted in the precipitation of the hydrochloride of unreacted 6-methoxy-8-aminoquinoline. The precipitate was filtered, washed with 10% hydrochloric acid solution, and dried (weight 4 g). To the mother liquor was added crystalline sodium acetate until the solution failed to show acid to Congo paper. The solution became turbid from the precipitation of traces of 6-methoxyaminoquinoline, which was extracted with ether. The aqueous solution was made alkaline with 10% sodium hydroxide solution and then extracted with ether; the extraction failed to remove a small amount of sticky black substance (0.6 g). The ether solution was washed with water and then dried over potash. After distilling off the ether there remained 12.7 g of fairly mobile brown liquid which was distilled in vacuo. At 120-125° (3-4 mm) there was collected 6.8 g of unreacted m-aminobenzyldiethylamine. The residue was distilled twice in vacuo and the fraction (1.8 g) boiling at 215-220° (3-4 mm) was collected. The yellow picrate was obtained by pouring together acetone solutions of the free base and picric acid. The picrate crystallized from acetone, and from water as tiny prisms. M.p. 242-243° (decompn.).

2.835 mg sub.: 0.421 ml N_2 (24°, 756 mm). 5.174 mg sub.: 0.784 ml N_2 (28°, 749 mm). Found %: N 16.98, 16.93. $C_{28}H_{22}O_{15}N_8$. Calculated %: N 17.10.

The picrate was converted to the free base, and the latter precipitated from ether in the form of pale yellow needles, m.p. 118°. Extremely soluble in alcohol, ether, and benzene; insoluble in water. The free base can be diazotized and coupled with β-naphthol.

3.042 mg sub.: 0.402 ml N_2 (20°, 753 mm). 2.107 mg sub.: 0.274 ml N_2 (18°, 751 mm). Found %: N 15.25, 15.07. $C_{17}H_{17}ON_3$. Calculated %: N 15.05.

b) The intimately ground mixture of 6-methoxy-8-aminoquinoline (8.7 g) and m-aminobenzyldiethylamine dihydrochloride (12.5 g) was heated in a sealed tube for 11 hours at 170-175°. The melt was dissolved in 10% hydrochloric acid solution, made alkaline, and extracted with ether. The ether failed to extract 1.3 g of dark brown substance, which was recrystallized from a mixture of benzene and petroleum ether. M.p. 168-170°; the mixed melting point of the obtained compound with 6-methoxy-8-(6'-methoxy-8'-quinolyl)aminoquinoline failed to show a depression. The residue after distilling off the ether was distilled in vacuo, and the fraction (0.4 g) boiling at 205-215° (3-4 mm) was collected.

8-(3'-Aminobenzyl)aminoquinoline

a) The intimately ground mixture of 8-aminoquinoline (7.2 g), m-aminobenzyldiethylamine free base (4.5 g) and m-aminobenzyldiethylamine dihydrochloride (6.3 g) was heated in a sealed tube for 18 hours at 170-175°. The obtained dark brown melt was dissolved in 10% hydrochloric acid solution, to the solution was added sodium acetate until it no longer showed acid to Congo paper, and the precipitate of unreacted 8-aminoquinoline was extracted with ether. Further treatment was the same as in the previous experiment. After distilling off the ether there was obtained 12.7 g of mobile brown liquid, which was distilled in vacuo. At 120-125° (3-4 mm) there was collected 7.3 g of unreacted m-aminobenzyldiethylamine. The residue was distilled twice in vacuo, and the fraction boiling at 215-225° (3-4 mm) was collected in an amount of 1.2 g.

The yellow picrate was obtained by pouring together acetone solutions of the free base and picric acid. The picrate crystallized from alcohol as tiny prisms with m.p. 235-236°.

3.520 mg sub.: 0.549 ml N_2 (20°, 750 mm). 3.400 mg sub.: 0.539 ml N_2 (19°, 750 mm). Found %: N 17.93, 18.29. $C_{28}H_{21}O_{14}N_9$. Calculated %: N 17.82.

The picrate was converted to the free base, and the latter crystallized from ether as white, slender needles. M.p. 125-126°.

The free base is extremely soluble in alcohol, ether and benzene; insoluble in water. It can be diazotized and coupled with β-naphthol.

2.795 mg sub.: 0.421 ml N_2 (19°, 737 mm). 2.884 mg sub.: 0.431 ml N_2 (19°, 737 mm). Found %: N 17.08, 16.94. $C_{16}H_{15}N_3$. Calculated %: N 16.87.

b) The intimately ground mixture of 8-aminoquinoline (4 g) and m-aminobenzyldiethylamine dihydrochloride (7 g) was heated in a sealed tube for 11 hours at 170-175°. Further treatment was the same as in the previous experiment. The ether extraction failed to remove 1.8 g of brownish product.

The residue after distilling off the ether was distilled in vacuo; the fraction (0.3 g) boiling at 210-225° (3-4 mm) was collected.

N-(3'-Aminobenzyl)-3-diethylaminomethylaniline

The liquid m-aminobenzyldiethylamine as the free base (4.8 g) and its solid dihydrochloride (6.5 g) were pasted in a mortar. The resulting thick, sticky, yellow mass solidified on grinding with the pestle, turned lighter in color and became friable. The mixture was heated in a sealed tube for 17 hours at 175-180°. On conclusion of heating, the reaction mixture appeared as a clear yellow melt, which was extracted by dissolving in 10% hydrochloric acid solution. The acid solution was made alkaline with 10% sodium hydroxide solution (a strong odor of diethylamine was detected when this was done), and the alkaline solution was extracted with ether. The ether solution was washed with water and then dried over potash. The residue after removal of the ether was distilled in vacuo: at 115-120° (3 mm) there was collected 5.2 g of original m-aminobenzyldiethylamine; at 225-230° (3 mm) there was obtained 1 g of pale yellow viscous liquid. The latter is readily soluble in alcohol, acetone, benzene and dilute acids, insoluble in water. n_D^{28} 1.5988.

2.909 mg sub.: 0.392 ml N_2 (28°, 750 mm). 1.887 mg sub.: 0.255 ml N_2 (29°, 751 mm). Found %: N 15.08, 15.09. $C_{11}H_{22}N_3$. Calculated %: N 14.84.

The white hydrochloride was obtained when dry HCl gas was passed into an ether solution of the free base. The hydrochloride is extremely hygroscopic. In a sealed capillary m.p. 91-94° (decompn.).

N-(3'-Aminobenzyl)-3-diethylaminomethylaniline

A mixture of m-aminobenzyldiethylamine (3.6 g) and m-nitrobenzyl chloride (3.4 g) was heated on the boiling water bath for 4 hours. The reaction mixture was dissolved in 10% hydrochloric acid solution, the solution was extracted with ether to remove unreacted m-nitrobenzyl chloride, then made alkaline with 10% sodium hydroxide solution, and extracted with benzene. The benzene solution was washed with water and then dried over potash. After removal of the solvent there remained 5 g of fairly mobile reddish liquid, the latter without further purification was catalytically (Raney nickel) reduced with hydrogen. The reduction product was distilled in vacuo: at 120-125° (4 mm) there was collected 1.1 g of unreacted m-aminobenzyldiethylamine; at 220-230° (3 mm) there was collected 1.3 g of viscous colorless liquid. The latter is readily soluble in alcohol, acetone, benzene and dilute acids; insoluble in water. n_D^{20} 1.5987.

3.305 mg sub.: 0.441 ml N_2 (27°, 756 mm). 3.624 mg sub.: 0.481 ml N_2 (22°, 750 mm). Found %: N 15.10, 15.16. $C_{18}H_{25}N_3$. Calculated %: N 14.84.

The white hydrochloride is extremely hygroscopic. In a sealed capillary m.p. 90-95° (decompn.). The mixed melting point with the hydrochloride of the N-(3'-aminobenzyl)-3-diethylaminomethylaniline obtained by the earlier described method fails to be depressed.

SUMMARY

1. A number of new compounds were synthesized: 6 methoxy-8-(3'-aminobenzyl)aminoquinoline, 8-(3'-aminobenzyl)aminoquinoline and N-(3'-aminobenzyl)-3-diethylaminomethylaniline.

2. The structure of N-(3'-aminobenzyl)-3-diethylaminomethylaniline was confirmed by its synthesis from m-nitrobenzyl chloride and m-aminobenzyldiethylamine with subsequent reduction of the nitro group.

3. The reaction between the free 6-methoxy- or 8-aminoquinoline and the hydrochloride of m-aminobenzyldiethylamine proceeds with the cleavage of diethylamine hydrochloride.

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β-AMINOFURANIDINE AND DIGLYCOLIC ACID FROM β-FURANIDONE

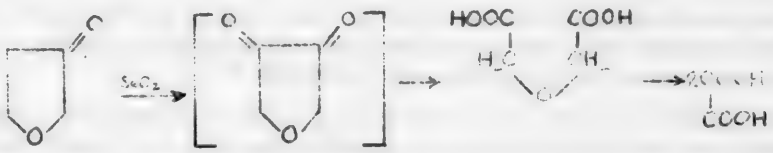
I. K. Korobitsyna, Yu. K. Yuryev, and E. M. Lukina

In our previous papers we described β-furanidone (tetrahydro-3-furanone) [1] and the preparation of β-alkyl- and β-arylfuranidones from it via the organomagnesium synthesis [2]. In the present paper other reactions of β-furanidone were studied: the preparation of β-aminofuranidine by reduction of the oxime, and also the oxidation with selenium dioxide under various conditions.

In the oxidation with selenium dioxide of ketones of the furanidine (tetrahydrofuran) series, possessing the carbonyl group in the 3 position and alkyl radicals in the 2,2,5,5-positions, the oxidation, directed toward the only methylene group in the ring, adjacent to the carbonyl group, proceeded smoothly, and the corresponding α-diketones, the 2,2,5,5-tetraalkyltetrahydro-3,4-furandiones, were obtained in excellent yields [3].

β-Furanidone, the base compound of the furanidine β-ketones, manifested a different behavior when oxidized with selenium dioxide. The oxidation in boiling dioxane (as was done in the oxidation of the 2,2,5,5-tetraalkyltetrahydro-3-furanones) was so profound that the oxidation products were oxalic acid and carbon dioxide; under milder temperature conditions, in boiling ether, the oxidation also proceeded with cleavage of the ring, but the oxygen bridge remained intact, and the oxidation product was diglycolic acid, although in this case also there was some formation of carbon dioxide, the complete oxidation product of the ketone.

As a result, in the oxidation of β-furanidone with selenium dioxide the oxidizing agent first of all attacks the methylene group, adjacent to the carbonyl group and occupying the 4-position in the furanidine ring, but the resulting tetrahydro-3,4-furandione is subjected to further oxidation, which leads to rupture of the ring at the carbon-carbon bond in the 3,4-position. The resulting diglycolic acid is oxidized further to oxalic acid, and the latter to carbon dioxide.



EXPERIMENTAL

The β-furanidone, used in the present study, had b.p. 139-140° (760 mm), n_D^{20} 1.4384, d_4^{20} 1.1240.

β-Furanidone thiosemicarbazone, obtained in quantitative yield from 1.5 g of the ketone in 10 ml of pyridine and 2.5 g of thiosemicarbazide hydrochloride in 3 ml of water, melted (after recrystallization from dilute alcohol) at 194-195°.

Found %: N 26.20, 26.26. $C_5H_9ON_3S$. Calculated %: N 26.40.

β-Furanidone oxime. To a solution of 28 g (0.4 mole) of hydroxylamine hydrochloride and 20 g (0.5 mole) of sodium hydroxide in 150 ml of water and 250 ml of alcohol in a flask with reflux condenser was added 20 g (0.23 mole) of β-furanidone. The mixture was heated for 2 hours on the boiling water bath. After neutralization with acetic acid and distilling off the solvent the residue was extracted with ether. The ether solution was washed with water and then dried over anhydrous sodium sulfate. After distilling off the ether the residue was distilled in vacuo. There was obtained 18.8 g of β-furanidone oxime (80% of the theoretical) as a colorless viscous liquid, which crystallized after standing for two days (not described in the literature): b.p. 78-78.5° (2 mm), m.p. 64-65°.

Found %: C 47.83, 47.65; H 7.11, 6.94; N 13.80, 14.07. $C_4H_7O_2N$. Calculated %: C 47.51; H 6.97; N 13.85.

β-Aminofuranidine. The β-furanidone oxime was reduced under the conditions described for the reduction of coumaranone oxime [4]. To a solution of 8 g (0.08 mole) of β-furanidone oxime in 150 ml of anhydrous alcohol

and 30 ml of glacial acetic acid in small portions and with stirring was added 400 g of 2.5% sodium amalgam. The reduction was run at 40-50° with the subsequent addition of another 15 ml of acetic acid so as to maintain an acid reaction medium. Then the reaction mixture was diluted with 100 ml of water, after which it was separated from the mercury. The aqueous solution was made alkaline and then extracted in the extractor for 20 hours with ether. After drying the ether extract over potash and distilling off the ether the residue was distilled in vacuo. There was obtained 2.3 g of unchanged oxime and 1.2 g of β-aminofuranidine (26%, calculated on reacted oxime):

B.p. 60-61° (30 mm), n_D^{20} 1.4591, d_4^{20} 1.0238, MR_D 23.16. C_4H_5ON. Calculated: 23.53.

β-Aminofuranidine is a colorless liquid with a characteristic amine odor, soluble in alcohol, ether, acetone and water (not described in the literature).

β-Furanidylbenzamide. To 0.5 g of benzoyl chloride in 10 ml of anhydrous benzene and 5 ml of pyridine in a flask with reflux condenser was added 0.5 g of β-aminofuranidine. After boiling the mixture for 30 minutes the cooled solution was filtered, washed with water, 5% potash solution, and dried. After distilling off the benzene and pyridine (in vacuo) the residue was recrystallized from benzene: m.p. 87-87.5°.

Found %: C 68.95, 69.14; H 7.05, 7.01; N 7.58, 7.47. $C_{11}H_{13}O_2N$. Calculated %: C 69.09; H 6.85; N 7.32.

β-Furanidyl-α-naphthylurea. To an ether solution of 0.2 g of β-aminofuranidine with stirring was added dropwise an equivalent amount of α-naphthyl isocyanate. After recrystallization from acetone the substance melted at 215-216°.

Found %: N 10.88, 11.01. $C_{15}H_{16}O_2N_2$. Calculated %: N 10.93.

α-Aminofuranidine picrate was precipitated in alcohol solution: m.p. (from alcohol) 151.5-152°.

Found %: N 17.51, 17.56. $C_{10}H_{12}O_7N_4$. Calculated %: N 17.72.

Oxidation of β-furanidone with selenium dioxide. a) To a boiling solution of 23.3 g (0.21 mole) of selenium dioxide in 200 ml of moist dioxane (in a 3-necked flask with stirrer, dropping funnel and reflux condenser, fitted with an escape tube descending into a solution of barium hydroxide) with stirring was added dropwise 17 g (0.2 mole) of β-furanidone, after which the mixture was heated for another 4 hours. A copious precipitate of barium carbonate collected in the test tube. Then the selenium was filtered, the dioxane was distilled, and the residue was extracted with ether. The ether extract was washed with a solution of sodium bicarbonate, water, and dried over anhydrous sodium sulfate. An insignificant amount of residue was obtained after distilling off the ether. The combined aqueous solutions were made alkaline and then evaporated to dryness. The solid residue was decomposed with dilute sulfuric acid, and the solution was extracted with ether. After drying the ether extract and distilling off the ether there was obtained 1 g of colorless crystals, which after recrystallization from water melted at 102° and were oxalic acid. The mixed melting point with known oxalic acid failed to show a depression.

b) To a boiling solution of 17 g (0.2 mole) of β-furanidone in 200 ml of ether (in the apparatus described above) was added with stirring a solution of 22 g (0.2 mole) of selenium dioxide in 10 ml of water. The reaction mixture was heated for 10 hours; the evolution of carbon dioxide was observed (by the precipitate of barium carbonate). Then the selenium was filtered and repeatedly washed with ether, and with water. The combined ether solution was washed with a solution of sodium bicarbonate and then dried over anhydrous sodium sulfate. After distilling off the ether and distilling the residue there was obtained 6.3 g of unchanged β-furanidone. The aqueous solution was treated in the above described manner. After distilling off the ether there was obtained 0.9 g of colorless crystals, showing acid reaction (to litmus) and melting (after recrystallization from water) at 141-142°.

Found %: C 36.08, 36.12; H 4.68, 4.53. $C_4H_6O_5$. Calculated %: C 35.82; H 4.48.

The analysis data for the obtained compound corresponded to diglycolic acid.

Literature data for diglycolic acid: m.p. 148° [5].

Authentic diglycolic acid, available to us, melted at 142-142.5°. The mixed melting point of the substance obtained by us with the authentic diglycolic acid failed to show a depression: m.p. 141-142°.

SUMMARY

1. The thiosemicarbazone and oxime of β-furanidone have been described, the reduction of the latter to β-aminofuranidine and the preparation of its derivatives – the picrate, β-furanidylbenzamide, and β-furanidyl-α-naphthylurea.

2. The oxidation of β-furanidone with selenium dioxide in dioxane at 100° leads to oxalic acid and carbon dioxide; the oxidation in boiling ether leads to the formation of diglycolic acid and carbon dioxide.

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* See Consultants Bureau Translation, page 191.

INVESTIGATIONS IN THE ANTHRAQUINONE SERIES

XXII. THE HYDROLYSIS OF α-ANTHRAQUINONYLMERCURY SULFATE

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The hydrolysis of α-anthraquinonylmercury chloride, described by us in a previous communication, revealed that the unsymmetrical arylmercury type of compound [1], appearing as the intermediate product in the sulfonation of anthraquinone in the presence of mercury, from its behavior can also serve as the intermediate product in the hydrolysis of α-anthraquinonesulfonic acid to anthraquinone [2]. However conclusive confirmation of this can be made only after studying the hydrolysis, not of α-anthraquinonylmercury chloride, but of α-anthraquinonylmercury sulfate, to which subject the present communication is devoted.

α-Anthraquinonylmercury sulfate was obtained by us from α-anthraquinonylmercury chloride by previously described methods [3]. The hydrolysis conditions and control of the process by the amount of separated mercury were analogous to those described in a previous communication* for the transformation of α-anthraquinonylmercury chloride.

The results on the hydrolysis of α-anthraquinonylmercury sulfate are given in Tables 1-7.

TABLE 1

Hydrolysis of $RHgSO_4H$ as a Function of Sulfuric Acid Concentration. (Time – 1 hour; 10 ml H_2SO_4)

Expt. No.	H_2SO_4 (in %)	$RHgSO_4H$ (in g)	KI consumed for 1 ml of solution (in ml)	Mercury found (in g)	Percent of hydrolyzed substance
			Temperature 190-195°		
1	25	0.0718	0.015	0.00106	4.3
2	40	0.0842	0.03	0.00212	7.0
3	50	0.1244	0.08	0.00566	13.0
4	60	0.1078	0.12	0.00849	22.5
5	75	0.0931	0.23	0.01628	50.0
6	85	0.0778	0.21	0.01487	54.6
7	100	0.1056	0.43	0.03058	98.0
			Temperature 170-175°		
8	50	0.1100	0.01	0.000708	1.8
9	60	0.1187	0.06	0.00415	9.9
10	75	0.1104	0.07	0.00521	13.2
11	85	0.1107	0.10	0.00708	18.0
12	100	0.1250	0.39	0.0276	63.0

Remarks. Here and later, T_{KI} 0.000708 g Hg.

First of all, from the experiments the great stability of α-anthraquinohylmercury sulfate when compared to α-anthraquinonylmercury chloride should be established. If RHgCl in 75% sulfuric acid at 190-195° for 1 hour is 90% hydrolyzed, then $RHgSO_4H$ under the same conditions is hydrolyzed a total of only 50% (Table 1). An even greater difference in the stability of the two compounds is observed at lower reaction temperatures. This stability of anthraquinonylmercury sulfate supports our earlier made postulation [3] (Tables 1 and 2).

As is known, the hydrolysis of α-anthraquinonesulfonic acid proceeds in the presence of mercury in 75-80% sulfuric acid at temperatures above 170° with the formation of anthraquinone. At temperatures below 170° the hydrolysis proceeds slowly [4]. The anthraquinone remaining from its sulfonation to the α-sulfonic acid and the

* Communication XXI – see J. Gen. Chem., 25, 410 (1955) [Consultants Bureau Translation, page 387].

TABLE 2

Hydrolysis of $RHgSO_4H$ as a Function of Time (Temperature 190-195°; 10 ml 75% H_2SO_4)

Expt. No.	Time (in minutes)	$RHgSO_4H$ (in g)	KI consumed for 1 ml of solution (in ml)	Mercury found (in g)	Percent hydrolyzed substance
1	30	0.1030	0.12	0.00849	23.5
2	60	0.0931	0.23	0.0163	50.0
3	120	0.1021	0.36	0.0255	72.3

TABLE 3

Influence of Mercury Sulfate Addition on the Hydrolysis of $RHgSO_4H$ (Temperature 190-195°; time – 1 hour; 10 ml H_2SO_4; 6% $HgSO_4$)

Expt. No.	H_2SO_4 (in %)	$RHgSO_4H$ (in g)	$HgSO_4$ (in g)	KI consumed for 1 ml of solution (in ml)	Mercury found (in g)	Percent hydrolyzed substance
1	25	0.0718	–	0.015	0.00106	4.3
2	25	0.1052	0.0059	0.07	0.00094*	2.2
3	50	0.1244	–	0.08	0.00566	13.0
4	50	0.1002	0.0066	0.13	0.0046*	8.0
5	75	0.0931	–	0.23	0.01628	50.0
6	75	0.0984	0.0050	0.16	0.00802*	23.2

TABLE 4

Influence of Chlorosulfonic Acid Addition on the Hydrolysis of $RHgSO_4H$ (Temperature 190-195°; time 1 hour; 10 ml H_2SO_4; 10% SO_2HCl)

Expt. No.	H_2SO_4 (in %)	SO_2HCl	$RHgSO_4H$ (in g)	KI consumed for 1 ml of solution (in ml)	Mercury found (in g)	Percent hydrolyzed substance
1	25	Absent	0.0718	0.015	0.00106	4.3
2	25	Present	0.1020	0.07	0.00496	14.0
3	50	Absent	0.1244	0.08	0.00566	13.0
4	50	Present	0.0972	0.13	0.0092	27.1
5	75	Absent	0.0931	0.23	0.01628	50.0
6	75	Present	0.1180	0.49	0.0377	84.2

anthraquinone formed in the hydrolysis of the sulfonic acid binds the mercury taken for sulfonation or hydrolysis into an organomercury compound of anthraquinone [5].

That the mercury is bound by the anthraquinone is also shown by the definite stability of the mercury compound of anthraquinone to aqueous sulfuric acid solutions at elevated temperatures; consequently, the relative stability of the pure compound in the form of the α-anthraquinonylmercury sulfate studied by us is not surprising. The hydrolysis of this compound in aqueous sulfuric acid is accompanied by the separation of a considerable amount of mercury, capable of retarding the hydrolysis process due to the reverse mercuration reaction:

$$RHgSO_4H + HOH \rightarrow RH + HgSO_4 \cdot HOH$$

$$HgSO_4 \cdot HOH(+ H_2SO_4) \rightleftharpoons HgSO_4 + HOH(+ H_2SO_4)$$

$$RH + HgSO_4 \rightarrow RHgSO_4H.$$

The lower degree of $RHgSO_4H$ hydrolysis when compared to RHgCl is due to the influence of the greater concentration of mercury sulfate or its hydrated amphoteric form $\left(HgSO_4 \cdot HOH = SO_2\begin{matrix}OHgOH\\OH\end{matrix}\right)$, which occurs specifically in the hydrolysis of $RHgSO_4H$. On introducing into the reaction during $RHgSO_4H$ hydrolysis a small amount of mercury sulfate (5-10% on the weight of substance) the degree of hydrolysis is lowered by 50% for almost all of the sulfuric acid concentrations (Table 3). This reduction is the result of the concurrent mercuration of anthraquinone. On the

* After subtracting the introduced mercury sulfate.

TABLE 5

Conversion of $RHgSO_4H$ in the Monohydrate as a Function of Temperature (Time 1 hour; 10 ml H_2SO_4)

Expt. No.	Temperature	$RHgSO_4H$ (in g)	KI consumed for 1 ml of solution (in ml)	Mercury found (in g)	Percent conversion
1	100°	0.1071	0.08	0.00566	15
2	120	0.0969	0.19	0.01345	40
3	140	0.0987	0.22	0.01557	45
4	170	0.1250	0.39	0.0276	63
5	190	0.1056	0.43	0.0306	98

other hand, the introduction into the reaction during $RHgSO_4H$ hydrolysis of a small amount of hydrochloric or chlorosulfonic acid (up to 10% on the weight of substance) accelerates the hydrolysis rate by 50% for almost all of the sulfuric acid concentrations (Table 4). The formation of the chloride ion in the reaction medium leads to the binding of the mercury as mercury chloride, which sublimes from the reaction sphere [5]. A decrease in the concentration of mercury sulfate quickly reduces the possibility of the anthraquinone mercuration reaction proceeding and, in reverse, accelerates the hydrolysis of $RHgSO_4H$ (Table 3).

The heating of $RHgSO_4H$ in the monohydrate also gave a different conversion picture when compared with the behavior of RHgCl. If the heating of RHgCl for 1 hour at 190° results in a cleavage of only 5%, then under the same conditions the cleavage of $RHgSO_4$ is practically complete (Table 5). The conversion of $RHgSO_4H$ in the monohydrate depends on the time, and especially on the temperature (Tables 5 and 6). The conversion of $RHgSO_4H$ in the monohydrate has a double direction. In one direction especially at comparatively low heating temperatures, the cleavage of the organomercury compound proceeds: $RHgSO_4H \rightleftharpoons RH + HgSO_4$. As can be seen from Table 6, up to 45% of the substance suffers cleavage in the first hour. Prolonging the heating time to 3 hours increases the amount of cleaved substance by only 20%. This retardation of cleavage with time is due to the establishment of the equilibrium cleavage-mercuration reaction. The introduction of mercury sulfate into the reaction medium also in the given case facilitates a reduction in the degree of substance cleavage, once again in favor of anthraquinone mercuration (Table 7).

TABLE 6

Conversion of $RHgSO_4H$ in the Monohydrate as a Function of Time (Temperature 140-145°; 10 ml H_2SO_4)

Expt. No.	Time (in minutes)	$RHgSO_4H$ (in g)	KI consumed for 1 ml of solution (in ml)	Mercury found (in g)	Percent conversion
1	30	0.0993	0.08	0.00566	16.0
2	60	0.0987	0.22	0.01557	45.0
3	120	0.0978	0.26	0.01840	54.2
4	180	0.1031	0.33	0.02336	65.0

TABLE 7

Influence of Sulfate Addition on the Conversion of $RHgSO_4H$ in the Monohydrate (Time 1 hour; 10 ml H_2SO_4; 10% $HgSO_4$)

Expt. No.	Temperature	$RHgSO_4H$ (in g)	$HgSO_4$ (in g)	KI consumed for 1 ml of solution (in ml)	Mercury found (in g)	Percent conversion
1	140°	0.0987	–	0.22	0.01557	45.0
2	140	0.1381	0.0143	0.31	0.01193*	24.8
3	170	0.1250	–	0.39	0.02760	63.0
4	170	0.1104	0.0122	0.42	0.05109*	58.0

In the other direction, especially on heating the substance in the monohydrate at 190°, together with cleavage of the substance there proceeds sulfonation of the liberated anthraquinone: $RH + H_2SO_4 \rightarrow RSO_3H\text{-}\beta + H_2O$.

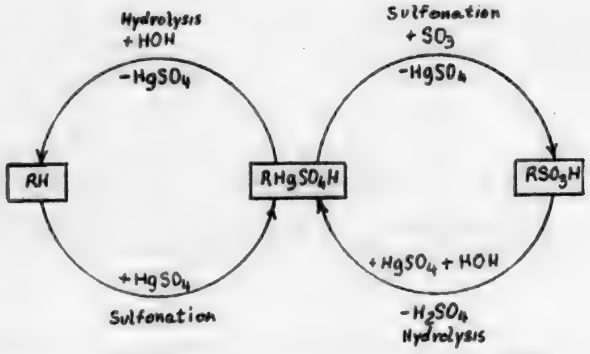
The sulfonation of anthraquinone under these conditions leads to the more stable β-anthraquinone sulfonic acid, identified by us by treating the sulfuric acid mother liquor (from heating $RHgSO_4H$ for 1 hour at 170° in the monohydrate) with potassium chlorate. The isolated chloroanthraquinone after recrystallization melted at 206° and failed to

* After subtracting the introduced mercury sulfate.

give a depression when mixed with pure β-chloroanthraquinone. It was established that α-chloroanthraquinone is present as impurity in the isolated crude chloroanthraquinone, indicating, as a result, that to a slight degree in the monohydrate it is possible at elevated temperature to suffer the transformation:

$$RHgSO_4H + H_2SO_4 \rightleftharpoons RSO_3H\text{-}\alpha + HOHgSO_4H.$$

In measure with anthraquinone (RH) removal, formed in the cleavage of $RHgSO_4H$, and its being bound as the β-sulfonic acid, the reaction for the cleavage of $RHgSO_4H$ in the monohydrate will always be shifted to the right. Because of this the rate for the transformation of $RHgSO_4H$ in the monohydrate will be higher than it is in aqueous sulfuric acid. The sulfonation of anthraquinone, formed in the cleavage of α-$RHgSO_4H$ by the monohydrate at 190-170°, supports the earlier observations made by a number of investigators relative to the analogous sulfonation of anthraquinone to the β-sulfonic acid during the hydrolysis of α-anthraquinonesulfonic acid in the presence of mercury [6]. The assertion of Lauer [7] on the impossibility of sulfonating anthraquinone with strong sulfuric acid at temperatures below 200° is not borne out in practice. The behavior of $RHgSO_4H$ when heated in different concentrations of sulfuric acid reveals that this mercury compound of anthraquinone is actually the intermediate product, not only in the sulfonation of anthraquinone in the presence of mercury to the α-sulfonic acid [1], but also in the hydrolysis of the α-sulfonic acid in aqueous sulfuric acid, also in the presence of mercury. This interrelationship can be depicted by the following scheme:



In common with the transformation of RHgCl and $RHgSO_4H$ to the sulfonic acid under the influence of SO_3 [1], and their hydrolysis in aqueous sulfuric acid solution, we observe a difference in their behavior when heated in the monohydrate. Most probably, the different stability of RHgCl and $RHgSO_4H$ in the monohydrate is associated with the structural characteristics of these two mercury compounds of anthraquinone.

EXPERIMENTAL

Study of the conversion of α-anthraquinonylmercury sulfate in the monohydrate at 170°. $RHgSO_4H$ (0.4558 g) was heated with 20 ml of the monohydrate in a round-bottomed flask with reflux condenser in an oil bath for 1 hour. The reaction mixture was poured over ice and the anthraquinone was filtered on a tared porous filter, washed with water until neutral to Congo paper, and dried at 100°.

There was obtained 0.027 g of product, which proved to be anthraquinone. The mother liquor with wash waters was transferred to a 100 ml volumetric flask. For 1 ml of this solution there was consumed 0.89 ml of KI solution (T_{KI} 0.00201 g Hg). Total mercury found was 36.69%, which is equal to about 100%, based on the amount of mercury in the taken weight of α-anthraquinonylmercury sulfate.

All of the remaining sulfuric acid solution was transferred to a three-necked flask fitted with mercury seal and reflux condenser, then 100 ml of water, 7 ml of 5 N hydrochloric acid and 2 g of potassium chlorate were added, and the mixture was heated for 2 hours at the boil. There was obtained 0.22 g of chloroanthraquinone, or 100%, calculated on the taken weight of $RHgSO_4H$.

The crude chloroanthraquinone melted at 198°, after recrystallization from acetic acid the m.p. was 206°, and no depression was observed when the compound was mixed with pure β-chloroanthraquinone.

SUMMARY

1. The hydrolysis of α-anthraquinonylmercury sulfate in different concentrations of sulfuric acid was studied. The most complete hydrolysis was obtained in 75-80% sulfuric acid at 170°. The hydrolysis is retarded by the addition

of mercury sulfate, due to the mercuration of anthraquinone, proceeding concurrently with the hydrolysis reaction.

2. It was established that the heating of α-anthraquinonylmercury sulfate at 170° in the monohydrate results in the cleavage of the substance into anthraquinone and mercury sulfate, while above 170° there occurs sulfonation of the formed anthraquinone to the β-sulfonic acid.

3. The behavior of $RHgSO_4H$ when heated in different concentrations of sulfuric acid permits accepting this substance as being the intermediate product in the hydrolysis of α-anthraquinonesulfonic acid in the presence of mercury and, as a result, expressing the complete interrelationship existing for the formation of α-anthraquinonesulfonic acid and its hydrolysis.

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ARYLSULFONAMIDOPHOSPHORYL BROMIDES

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The hydrolysis of tribromophosphazosulfonaryls when treated with water proceeds easily with the formation of the dibromides, the monobromides and the free arylsulfonamidophosphoric acids in accord with the scheme:

$$ArSO_2N{=}PBr_3 + H_2O \rightarrow HBr + ArSO_2NHPOBr_2,$$

$$ArSO_2NHPOBr_2 + H_2O \rightarrow HBr + ArSO_2NHPO(OH)Br,$$

$$ArSO_2NHPO(OH)Br + H_2O \rightarrow HBr + ArSO_2NHPO(OH)_2.$$

Phosphoric acid and the corresponding arylsulfamide are formed on further hydrolysis. Although the isolation of the intermediate products is possible, such isolation is associated with great experimental difficulties, since the rates of all three reactions differ but slightly between themselves; consequently, to obtain the arylsulfonamidophosphoryl bromides a method was chosen that had been successfully used earlier for the preparation of the arylsulfonamidophosphoryl chlorides, namely, by the action of anhydrous formic acid on the corresponding trihalophosphazo compounds [1], proceeding in accord with the scheme:

$$ArSO_2N{=}PBr_3 + HCOOH \rightarrow ArSO_2NHPOBr_2 + HBr + CO,$$

$$ArSO_2NHPOBr_2 + HCOOH \rightarrow ArSO_2NHPO(OH)Br + HBr + CO,$$

$$ArSO_2NHPO(OH)Br + HCOOH \rightarrow ArSO_2NHPO(OH)_2 + HBr + CO.$$

The first two reactions proceed readily in benzene solution at room temperature or with moderate heating; the third reaction proceeds at the boil in benzene solution.

The arylsulfonamidophosphoryl monobromides and dibromides are colorless crystalline compounds, comparatively stable toward atmospheric moisture, and easily and completely hydrolyzed when treated with boiling water. They readily react with alcohols, alcoholates, amines, phenols and other substances containing an active hydrogen. The free arylsulfonamidophosphoric acids, as was to be expected, proved to be identical with the substances obtained by the acidolysis of the arylsulfonamidophosphoryl chlorides [2].

All of the arylsulfonamidophosphoryl bromides melt with decomposition. With very slow heating sintering of the compounds is observed several degrees below the beginning of melting.

All of the acid bromides are readily soluble in ether and hot benzene, less readily in chloroform, and slightly soluble in carbon tetrachloride and cold benzene.

The free arylsulfonamidophosphoric acids are readily soluble in water and alcohol, insoluble in ether, benzene, chloroform and carbon tetrachloride.

EXPERIMENTAL

Preparation of the dibromides, monobromides and free arylsulfonamidophosphoric acids. The tribromophosphazosulfonaryl (0.01 mole) was dissolved in 10-25 ml of benzene, with heating if necessary, and 0.01, 0.02 or 0.03 mole of anhydrous formic acid was added. To obtain the dibromides the reaction mixture was heated for 1 hour on the water bath at 80°, to obtain the monobromides the mixture was heated for 2 hours, and to obtain the free acids – by heating for 4 hours. The fairly vigorous evolution of carbon monoxide and hydrogen bromide began soon after the addition of the formic acid, and the reaction product was deposited as well formed crystals or as an oily layer, which quickly became crystalline.

After conclusion of heating the reaction mixture was allowed to stand for a day at room temperature, the reaction product was suction filtered, washed with benzene, and recrystallized from hot benzene. In preparing the acid bromides it was necessary to protect the reaction mixture and reaction products from the action of atmospheric moisture.

As a result, there were obtained:

Phenylsulfonamidophosphoryl dibromide, $C_6H_5SO_2NHPOBr_2$, yield 90.9%, fine prisms, m.p. 122-124° (begins to sinter at 119°).

Found %: Br 44.42. Equivalents after hydrolysis, 4.03. $C_6H_6SO_3NPBr_2$. Calculated %: Br 44.03. Equivalents after hydrolysis 4.00.

Phenylsulfonamidophosphoryl monobromide, $C_6H_5SO_2NHPO(OH)Br$, yield 82.3%, crystallizes as needles, m.p. 147-150° (sinters 145°).

Found %: Br 25.95. Equivalents after hydrolysis 3.08. $C_6H_7SO_4NPBr$. Calculated %: Br 26.30. Equivalents after hydrolysis 3.00.

Phenylsulfonamidophosphoric acid, $C_6H_5SO_2NHPO(OH)_2$, yield 76.0%, fine prisms, m.p. 147-148°.

Found: equiv. 197. $C_6H_8SO_5NP$. Calculated: equiv. 2.00.

o-Tolylsulfonamidophosphoryl dibromide, o-$CH_3C_6H_4SO_2NHPOBr_2$, yield 74.2%, flat prisms, m.p. 123-126° (begins to sinter at 118°).

Found %: Br 42.45. Equivalents after hydrolysis 4.03. $C_7H_8SO_3NPBr_2$. Calculated %: Br 42.39. Equivalents after hydrolysis 4.00.

o-Tolylsulfonamidophosphoryl monobromide, o-$CH_3C_6H_4SO_2NHPO(OH)Br$, yield 71.0%, needles, m.p. 126-129° (begins to sinter at 122°).

Found %: Br 25.96. Equivalents after hydrolysis 3.01. $C_7H_9SO_4NPBr$. Calculated %: Br 25.44. Equivalents after hydrolysis 3.00.

o-Tolylsulfonamidophosphoric acid, o-$CH_3C_6H_4SO_2NHPO(OH)_2$, yield 86.4%, crystalline powder, m.p. 139-141°.

Found: equiv. 2.07. $C_7H_{10}SO_5NP$. Calculated: equiv. 2.00.

p-Tolylsulfonamidophosphoryl dibromide, p-$CH_3C_6H_4SO_2NHPOBr_2$, yield 90.7%, fine prisms, m.p. 123-126° (begins to sinter at 118°).

Found %: Br 42.53. Equivalents after hydrolysis 4.02. $C_7H_8SO_3NPBr_2$. Calculated %: Br 42.39. Equivalents after hydrolysis 4.00.

p-Tolylsulfonamidophosphoryl monobromide, p-$CH_3C_6H_4SO_2NHPO(OH)Br$, yield 85.7%, crystalline powder, m.p. 137-140° (begins to sinter at 132°).

Found %: Br 24.98. Equivalents after hydrolysis 3.00. $C_7H_9SO_4NPBr$. Calculated %: Br 25.44. Equivalents after hydrolysis 3.00.

p-Tolylsulfonamidophosphoric acid, p-$CH_3C_6H_4SO_2NHPO(OH)_2$, yield 89.0%, fine cubic crystals, m.p. 151-153°.

Found: equiv. 2.00. $C_7H_{10}SO_5NP$. Calculated: equiv. 2.00.

α-Naphthylsulfonamidophosphoryl dibromide, α-$C_{10}H_7SO_2NHPOBr_2$, yield 84.7%, fine prisms, m.p. 131-134° (begins to sinter at 126°).

Found %: Br 38.27. Equivalents after hydrolysis 3.97. $C_{10}H_8SO_2NPBr_2$. Calculated %: Br 38.69. Equivalents after hydrolysis 4.00.

α-Naphthylsulfonamidophosphoryl monobromide, α-$C_{10}H_7SO_2NHPO(OH)Br$, yield 77.1%, prisms, m.p. 127-130° (begins to sinter at 122°).

Found %: Br 22.31. Equivalents after hydrolysis 3.00. $C_{10}H_9SO_4NPBr$. Calculated %: Br 22.82. Equivalents after hydrolysis 3.00.

α-Naphthylsulfonamidophosphoric acid, α-$C_{10}H_7SO_2NHPO(OH)_2$, yield 74.5%, fine prisms, m.p. 159-161°.

Found: equiv. 2.01. $C_{10}H_{10}SO_5NP$. Calculated: equiv. 2.00.

β-Naphthylsulfonamidophosphoryl dibromide, β-$C_{10}H_7SO_2NHPOBr_2$, yield 80.4%, prisms, m.p. 161-163° (begins to sinter at 159°).

Found %: Br 38.63. Equivalents after hydrolysis 3.94. $C_{10}H_8SO_2NPBr_2$. Calculated %: Br 38.69. Equivalents after hydrolysis 4.00.

β-Naphthylsulfonamidophosphoryl monobromide, β-$C_{10}H_7SO_2NHPO(OH)Br$, yield 89.7%, prisms, m.p. 163-165°.

Found %: Br 22.76. Equivalents after hydrolysis 3.03. $C_{10}H_9SO_4NPBr$. Calculated %: Br 22.86. Equivalents after hydrolysis 3.00.

β-Naphthylsulfonamidophosphoric acid, β-$C_{10}H_7SO_2NHPO(OH)_2$, yield 84.0%, fine prisms, m.p. 174-175°.

Found: equiv. 2.00. $C_{10}H_{10}SO_5NP$. Calculated: equiv. 2.00.

SUMMARY

The acidolysis of tribromophosphazosulfonaryls with formic acid was studied. The acid dibromides, monobromides and free arylsulfonamidophosphoric acids were prepared and described.

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THE OXIDATION OF BENZALDEHYDE AND BENZYL CHLORIDE WITH PERHYDROL

V. P. Golendeev

The purpose of the present work was the possible rapid oxidation of benzaldehyde and benzyl chloride to benzoic acid and the isolation of the latter in pure form. It was revealed that benzaldehyde and benzyl chloride are very rapidly oxidized to benzoic acid by perhydrol in alkaline medium in the presence of a small amount of potassium permanganate as catalyst. The reaction is completed in approximately an hour if the perhydrol is added dropwise to the reaction mixture. The formation of a clear solution of the sodium salt of benzoic acid serves as the process control. The benzoic acid is then separated from the solution by the addition of 10-15% hydrochloric acid, and is recrystallized. The oxidation proceeds so vigorously that frequently it becomes necessary to retard the reaction by cooling with cold water.

The known method for the preparation of benzoic acid from benzaldehyde by the Cannizzaro reaction of oxidation-reduction under the influence of potassium hydroxide [1] is also associated with the formation of benzyl alcohol, both the latter and benzoic acid being formed in this reaction. However, the oxidation-reduction reaction proceeds at a slow rate and requires more than ten hours for its completion. The proposed method for the oxidation of benzaldehyde and benzyl chloride with perhydrol possesses independent significance. This method of oxidation by perhydrol with the aid of a manganese catalyst can find use for many oxidation processes.

The role and action mechanism of the manganese catalyst in the oxidation reaction with perhydrol is an extremely interesting problem. In the literature it is indicated [2] that the action of the catalyst essentially consists in the transfer of oxygen to the substance being oxidized by the manganese oxides that are formed under the reaction conditions. For example:

$$Mn_2O_3 + H_2O_2 \rightarrow 2MnO_2 + H_2O$$

$$2MnO_2 + R{-}COH \rightarrow Mn_2O_3 + R{-}COOH, \text{ etc.}$$

However, in the deoxidation of the perhydrol, as can be observed by the change in the color of the reaction solution (from brown to green), apparently in the given case the manganese oxides with a higher degree of oxidation also participate in the oxidation process. For example:

$$MnO_2 + H_2O_2 \rightarrow MnO_3 + H_2O$$

$$MnO_3 + C_6H_5{-}COH \rightarrow MnO_2 + C_6H_5{-}COOH, \text{ etc.}$$

It is possible in this manner to explain the extremely rapid oxidation rate obtained with perhydrol in the presence of a manganese catalyst.

EXPERIMENTAL

In the study of the oxidation reaction with perhydrol it was necessary to establish the optimum conditions for the process, and specifically, the most suitable quantitative proportions of reactants for a given oxidation time (45 minutes) and a given amount of oxidized substance (4 g of benzaldehyde). For this separate experiments were set up to determine the influence of the amounts of perhydrol and catalyst on the reaction rate. In the experiments to determine the influence of the amounts of perhydrol on the oxidation reaction, the benzaldehyde was taken in an amount of 4 g, while the catalyst was taken in an amount of 0.5 ml (7% aqueous potassium permanganate solution). The amount of perhydrol was varied from 25 to 40 ml. Complete oxidation was achieved in 45 minutes when 40 ml of oxidizing agent was used for 4 g of substance.

In the experiments to determine the influence of the catalyst the amount of catalyst was varied from 0.1 to 0.5 ml with the amounts of benzaldehyde (4 g) and perhydrol (35 ml) kept constant. Time, 45 minutes. It was found that the optimum amount of catalyst was about 0.3 and 0.4 ml for 4 g of benzaldehyde.

Parallel experiments on the oxidation of benzyl chloride revealed that the perhydrol is consumed twice as fast, in which connection the oxidation time is prolonged 3-fold. On the basis of the presented experiments on the oxidation of benzaldehyde with perhydrol the following method is proposed for the preparation of benzoic acid.

The mixture, composed of 4 g of benzaldehyde, 5 g of 50% potassium hydroxide solution and 0.3-0.4 ml of catalyst (an aqueous 6-8% potassium permanganate solution), is charged into a flask fitted with a reflux air condenser and a dropping funnel, the latter conthining 35 ml of perhydrol. The perhydrol is added dropwise to the reaction mixture. The reaction begins in the cold and proceeds with great vigor. Already within 40-45 minutes the benzaldehyde is almost completely oxidized to benzoic acid and the reaction solution becomes clear. The unreacted benzaldehyde is removed by heating the reaction mixture at the boil until the odor of benzaldehyde has disappeared. The obtained benzoic acid is precipitated by the addition of 10-15% hydrochloric acid, filtered, and recrystallized from alcohol. The yield is about 4 g. The melting point of the obtained benzoic acid is 121°.

SUMMARY

1. A new method is proposed for the oxidation of organic compounds with perhydrol in the presence of a manganese catalyst.

2. On the basis of this proposal a method was developed for obtaining benzoic acid by the catalytic oxidation of benzaldehyde and benzyl chloride with perhydrol.

3. The given method has an advantage over other methods in the oxidation rate, simplicity, and reaction efficiency.

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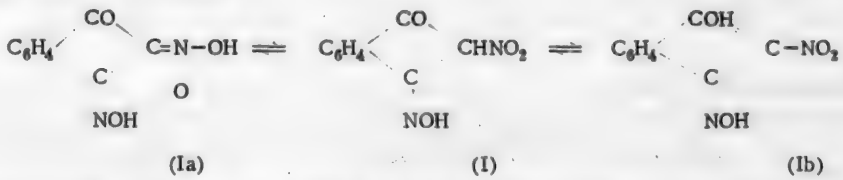
SALTS OF 2-NITRO-1,3-INDANDIONE OXIME

V. N. Vitol and G. Ya. Vanag

Nitroindandione oxime (I) had already been obtained earlier by the action of hydroxylamine on 2-nitro-1,3-indandione, and its properties had been partially studied [1, 2]. Nitroindandione oxime is a yellow crystalline substance with m.p. 152-153°. At room temperature it is slightly soluble in water and in organic solvents; its solubility is noticeably increased on heating.



(Ia) (I) (Ib)

Nitroindandione oxime is a fairly strong acid and consequently readily lends itself to salt formation. Since the nitroindandione salts possess certain valuable analytical properties it appeared interesting to study the manner in which these properties are changed by the introduction of the oxime group into the nitroindandione molecule. Although the nitroindandione oxime molecule has two hydrogen atoms that are capable of being replaced by metal, nevertheless, nitroindandione oxime for the most part behaves as a monobasic acid. If salts with two univalent metal atoms are formed by the action of excess alkali, then they are unstable and their isolation in the pure state proved impossible.

Also still unanswered remains the question of the form in which the nitroindandione oxime lends itself to salt formation. For, in addition to structure (I), the oxime can also react in the form of the nitronic acid (Ia) and in the enol form (Ib). The nitroindandione salts for the most part are derived from the nitronic acid form [6, 7], but without sufficient evidence it is impossible to transfer this to the nitroindandione oxime. It is characteristic that the sodium and potassium salts of the nitroindandione oxime, especially if an excess of alkali or methylate is used, can be obtained as red crystals; however, these red salts are unstable and they quickly transform into stable yellow salts, the color of which differs but slightly from the color of the nitroindandione oxime. Other colorless cations give only the yellow salts.

Many of the nitroindandione oxime salts proved to be quite difficultly soluble in water and in alcohol. Thus, for example, the solubility of the sodium and potassium salts in cold water is approximately 0.5%, while in alcohol, it is even less. The solubility of the ammonium salt in water is only about 0.2%. The magnesium salt crystallizes with 7 mols of water and its solubility in water is approximately 0.5%.

It appeared desirable to prepare some other more readily soluble salt of the nitroindandione oxime, which could be used as a reagent for the precipitation of other salts. For this the salts of the nitroindandione oxime with organic bases were investigated. For the most part these salts were prepared by the method of treating the suspension of the nitroindandione oxime in water or alcohol with the corresponding base; here the nitroindandione oxime, usually failing to dissolve completely, was converted into the corresponding salt. Heating on the water bath accelerated this conversion.

The nitroindandione oxime salts with amines for the most part give well-formed crystals with fairly sharp melting points. The solubility of many of the nitroindandione oxime salts with organic bases proved to be extremely low, so that the nitroindandione oximes can be used for the isolation and identification of many organic bases. An especially low solubility is shown by the salts of primary amines, even the first members of the aliphatic series. It appears that often these salts are one of the least soluble simple salts of these aliphatic amines. The salts of the secondary amines are somewhat more soluble in water. The trimethylamine salt of the nitroindandione oxime proves to be very slightly soluble in water; in contrast, the solubility of the triethylamine salt in water is about 10%. Some of the other tertiary amine salts are also quite readily soluble, and also the ethanolamine salts.

The piperidine salt is quite readily soluble in water. An excess of piperidine, similar to the alkalies, gives an orange solution. The pyridine salt is less soluble, and even less soluble are the quinoline and isoquinoline salts (see Table). Some of the alkaloid salts also possess a fairly low solubiltiy.

The nitroindandione oxime salts that are readily soluble in water, for example, the triethylamine salt, give precipitates with an extremely large number of amine salts and other nitrogen bases, which as a result, can be easily isolated. The salts dissolve in alkali, giving orange solutions, and when they are acidified the unchanged nitroindandione oxime is precipitated.

If a hot alcohol solution of the nitroindandione oxime is allowed to cool and the resulting precipitate is filtered, then the filtrate contains 0.2-0.25% of the nitroindandione oxime. If a small amount of base is added to such a solution, then yellow crystalline precipitates are given by: methylamine, ethylamine, n-butylamine, n-amylamine, β-phenylisopropylamine, cyclohexylamine and ethylenediamine, and also by aniline, toluidines, xylidines, phenylenediamines and other aromatic primary amines; crystalline precipitates are also given by the secondary amines: dimethyl-, n-dipropyl-, n-dibutyl-, diisobutyl-, diamyl- and dicyclohexylamine, and also by N-methyl-, ethyl- and propylaniline. Phenylhydrazine and hydrazine also give crystalline precipitates. Precipitates are not given by trimethyl-, triethyl- and triisobutylamine, by mono-, di- and triethanolamine, and also by pyridine, quinoline, isoquinoline, quinaldine and piperidine.

TABLE

Salts of Nitroindandione Oxime with Amines

Amine	Salt composition	Nitrogen (%) found	Nitrogen (%) calculated	Melting point	Approximate solubility of the salt in water at room temperature (g in 100 ml)
Methylamine	$C_{10}H_{11}O_4N_3$	17.67	17.72	205°	0.07
Ethylamine	$C_{11}H_{13}O_4N_3$	16.94	16.74	222-224	0.13
Propylamine	$C_{12}H_{15}O_4N_3$	15.70	15.83	226-227	0.04
n-Butylamine	$C_{13}H_{17}O_4N_3$	15.52	15.05	210-211	0.09
Dimethylamine	$C_{11}H_{13}O_4N_3$	16.73	16.73	206-207	0.2
Diethylamine	$C_{13}H_{17}O_4N_3$	15.18	15.05	212-213	0.3
Di-n-propylamine	$C_{15}H_{21}O_4N_3$	13.87	13.69	224-225	0.07
Diisobutylamine	$C_{17}H_{25}O_4N_3$	12.33	12.53	228-229	
Trimethylamine	$C_{12}H_{15}O_4N_3$	15.62	15.85	> 265	0.01
Triethylamine	$C_{15}H_{21}O_4N_3$	13.91	13.68	80-83	10
Triisobutylamine	$C_{21}H_{33}O_4N_3$	10.85	10.75	142-143	0.2
Ethylenediamine	$C_{20}H_{20}O_8N_6$	17.35	17.80		0.005
Aniline	$C_{15}H_{13}O_4N_3$	14.37	14.05	205	0.05
p-Toluidine	$C_{16}H_{15}O_4N_3$	13.79	13.42		
m-Xylidine	$C_{17}H_{17}O_4N_3$	13.20	12.84		
m-Phenylenediamine	$C_{24}H_{20}O_8N_6$	16.15	16.15	194	
Benzidine	$C_{21}H_{15}O_4N_4$	14.35	14.35		
Pyridine	$C_{14}H_{11}O_4N_3$	14.73	14.74	223-224	0.1
Piperidine	$C_{14}H_{17}O_4N_3$	14.28	14.43	183-184	0.2
Quinoline	$C_{19}H_{13}O_4N_3$	12.69	12.54	146	0.02
Isoquinoline	$C_{19}H_{13}O_4N_3$	12.73	12.54	145-146	0.03
Conitine	$C_{17}H_{23}O_4N_3$	12.40	12.61	135-136	0.02
Nicotine	$C_{19}H_{22}O_4N_4$	14.88	15.23	142-143	0.01

If the nitroindandione oxime salt with some of the tertiary amines is heated for a longer time in alcohol or water solution, then the salt suffers a change and is transformed into a less soluble substance, containing a considerably larger amount of nitrogen; for example, the triisobutylamine salt of the nitroindandione oxime has a nitrogen content of 10.75%, while after it has been boiled a substance is obtained with a nitrogen content of 15.50%; the isoquinoline salt before boiling contains 12.54% nitrogen, after boiling the nitrogen content is 17.00%, etc.. The nature of this transformation has not yet been determined.

EXPERIMENTAL

Inorganic Salts of 2-Nitro-1,3-indandione Oxime

Sodium salt. The finely divided nitroindandione (1.2 g) was covered in a porcelain dish with 15 ml of freshly prepared 3% sodium methylate solution. The yellow oxime was transformed into the bright red sodium salt. Stirring

was continued until a completely homogeneous mixture was obtained. The product was filtered, washed with alcohol, dissolved in the least possible amount of water, and the sodium salt was precipitated by the addition of alcohol to the filtrate. Yellow needles of the monosodium salt of the nitroindandione oxime were precipitated from the orange-red solution when the alcohol was added. The compound is practically insoluble in organic solvents.

The salt can also be obtained by dissolving the oxime in an aqueous solution of pure sodium hydroxide.

0.1026 g sub.: 0.0314 g Na_2SO_4. 4.129 mg sub.: 0.429 ml N_2 (23°, 764 mm). Found %: Na 9.92; N 12.05. $C_9H_5O_4N_2Na$. Calculated %: Na 10.08; N 12.29.

Potassium salt. The nitroindandione oxime was boiled with a 1% aqueous potassium hydroxide solution until it was almost completely dissolved. The solution was colored orange-red. Cooling of the filtrate gave the potassium salt as plate crystals. The salt is practically insoluble in organic solvents. When heated in a test tube, the dry salt decomposes with frothing and flashing.

0.0738 g sub.: 0.0270 g K_2SO_4. 2.514 mg sub.: 0.246 ml N_2 (18°, 749 mm). Found %: K 16.42; N 11.31. $C_9H_5O_4N_2K$. Calculated %: K 16.01; N 11.48.

Magnesium salt. A mixture of 2 g of the nitroindandione oxime and 1 g of magnesium oxide was covered with water and boiled for 20 minutes. Part of the substance dissolved. Cooling of the filtrate gave the magnesium salt as yellow needle crystals, containing 7 mols of water of crystallization. On drying at 55°, the salt loses 4 mols of water; at 90-110°, the salt loses all of its water of crystallization. The salt is practically insoluble in organic solvents.

0.2014 g sub.: 0.0460 g $MgSO_4$. 2.586 mg sub.: 0.220 ml N_2 (16°, 767 mm). 0.3914 g sub. at 90-110° the loss in water 0.0866 g. Found %: Mg 4.62; N 10.14; H_2O 22.13. $C_{18}H_{18}O_8N_4Mg \cdot 7H_2O$. Calculated %: Mg 4.34; N 10.01; H_2O 22.50.

Ammonium salt. The nitroindandione oxime dissolves with difficulty in concentrated ammonia on heating. From the yellow solution on cooling the ammonium salt precipitates as needle crystals with m.p. 215-217°. The salt can be recrystallized from alcohol; in other organic solvents the salt is practically insoluble. On boiling in glacial acetic acid the salt decomposes: the solution acquires a dark brown color, and neither the ammonium salt nor the nitroindandione oxime can any longer be isolated from this solution.

4.014 mg sub.: 0.615 ml N_2 (13°, 773 mm).. Found %: N 18.61. $C_9H_6O_4N_2$. Calculated %: N 18.84.

Organic Salts of Nitroindandione Oxime

These salts were usually prepared by treating a suspension of the nitroindandione oxime in alcohol or water with the corresponding amine, or by the method of precipitating the amine salt with some other more soluble nitroindandione oxime salt, for example, the triethylamine or sodium salt, so that for the sake of illustration we will limit ourselves to only a few examples. The analysis results, melting points, solubility, etc., are given in the Table.

Methylamine salt. a) A mixture of 1 g of nitroindandione oxime, 15 ml of alcohol and a slight excess of aqueous 33% methylamine solution was heated to the boil on the water bath and then allowed to stand until the following day. All of the nitroindandione oxime was transformed into the yellow methylamine salt. The salt crystallizes from water in the form of needles. It is more difficultly soluble in alcohol than in water, and is practically insoluble in other organic solvents.

b) To an aqueous solution of methylamine hydrochloride was added an aqueous solution of the triethylamine salt of the nitroindandione oxime. The light yellow crystalline methylamine salt of the nitroindandione oxime was obtained in this manner.

Triethylamine salt. a) To a suspension of 5 g of the nitroindandione oxime in alcohol was added 4 ml of triethylamine and the mixture heated on the water bath. The oxime almost completely dissolved to give a yellow solution. Ether was gradually added to the cooled filtrate. The triethylamine salt was obtained as light yellow needle crystals.

b) The nitroindandione oxime was suspended in water and an excess of triethylamine was added. The oxime went into solution. With slight heating more of the nitroindandione oxime was added to the solution until it began to dissolve with difficulty. On the following day, the light yellow crystals of the triethylamine salt were isolated from the filtered solution.

SUMMARY

A number of inorganic and organic salts of 2-nitro-1,3-indandione oxime were prepared. Many organic bases with nitroindandione oxime give slightly soluble salts, which fact can be used for the isolation and identification of

various amines. The salts of primary aliphatic amines are characterized by a low solubility. The salts of secondary amines are somewhat more soluble. The salts of tertiary amines are even more soluble. An exception is the trimethylamine salt which has a very poor solubility, whereas the triethylamine salt is one of the most soluble salts of nitroindandione oxime. The salts of some of the heterocyclic compounds and alkaloids are characterized by a fairly low solubility.

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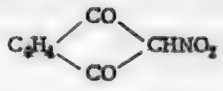
* See Consultants Bureau Translation, page 1551.

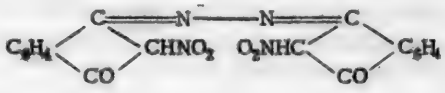
2-NITRO-1,3-INDANDIONE AZINE

G. Ya. Vanag and M. A. Matskanova

Hydrazine has two primary amino groups, and the amines, especially primary amines, with 2-nitro-1,3-indandione (I) give slightly soluble crystalline salts [1-4]; consequently, if a solution of the hydrazine salt is added to a solution of the nitroindandione there is obtained a yellow crystalline precipitate. Depending on the conditions, it is possible to obtain the hydrazine nitroindandionates with either one or two moles of the nitroindandione. When heated the precipitate goes into solution, but on boiling the yellow solution it first begins to turn orange, and then red, and on cooling an orange-red precipitate is obtained. The same thing also happens in alcohol solution.



(I)



(II)

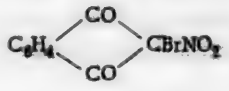
The nitroindandione (I) contains two carbonyl groups, and hydrazine, as is known, readily condenses with such compounds, forming the corresponding hydrazones; consequently, here also we could expect the formation of the nitroindandione hydrazone. However, it was revealed that in an acid solution with an excess of the nitroindandione the nitroindandione azine (II) is always formed, as is also frequently observed in the case of other ketones. Under no circumstances were we able to condense both of the keto groups in the nitroindandione with hydrazine, similar to the situation with hydroxylamine where only the nitroindandione monoxime is always formed [5].

Nitroindandione azine is an orange-red substance and melts at 225-230° (with decompn.). Under rapid heating the dry substance decomposes violently with frothing. Nitroindandione azine is somewhat soluble in water, acetone and formic acid, and slightly soluble in other organic solvents. The azine can be precipitated from its acetone solution with petroleum ether. From aqueous solutions the azine can be precipitated by different inorganic salts. For example, sodium chloride completely precipitates the azine from a water solution, in which connection a finely crystalline red precipitate with m.p. 287-290° is obtained, containing, besides the nitroindandione azine, also sodium chloride and water, and corresponding to the formula $C_{18}H_{10}O_6N_4 \cdot NaCl \cdot 2H_2O$. The substance on drying loses its water of crystallization. The azine can also be precipitated with concentrated mineral acids.

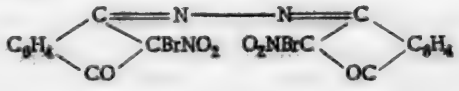
The azine is readily soluble in dilute alkalies, forming yellow solutions; when these solutions are acidified the unchanged azine is recovered. From this it follows that, together with the nitro group, the active hydrogen grouping is retained.

When reduced with zinc dust, the solution of the azine in glacial acetic acid gives a purple color with bindone, which indicates reduction of the nitro group to the amino group [6]. Only phthalic acid was obtained when the azine was subjected to oxidation.

The nitroindandione is readily brominated [1] with the formation of 2-bromo-2-nitro-1,3-indandione (III). It was revealed that the nitroindandione azine is also readily brominated with the formation of the bromonitroindandione azine (IV). The validity of the given formula is confirmed by the fact that the same substance is also obtained by the action of hydrazine on the bromonitroindandione (III).



(III)



(IV)

The bromonitroindandione azine (IV) is a yellow substance with m.p. 218°. The bromine atom in the molecule is extremely labile and in many respects is reminiscent of the bromine atom in the bromonitroindandione. Thus, for example, a suspension of the bromonitroindandione azine in water acquires the odor of hypobromous acid, and separates iodine from potassium iodide solution. Vapors with an acrid odor (bromonitromethane) are evolved when the bromonitroindandione azine is heated in concentrated sulfuric acid, and needles of phthalic anhydride sublime on the

walls of the test tube. When heated in xylene or nitrobenzene the bromonitroindandione azine decomposes to ninhydrin (indantrione hydrate), the same thing as happens with the bromonitroindandione [7]. The bromonitromethane, which is also formed in the decomposition of the bromonitroindandione [8], distills off when the solvent is removed by steam distillation.

Since hydroxylamine in acid solution gives only the yellow nitroindandione oxime [5], and its presence with an excess of the nitroindandione fails to interfere with the formation of the orange-red nitroindandione azine, this reaction can be used for detecting hydrazine in the presence of hydroxylamine, for which up to the present there fail to exist any specific color reactions [9]. A detailed description of this analytical use for the nitroindandione will be given separately.

EXPERIMENTAL

2-Nitro-1,3-indandione azine. To a solution of 3.8 g of the nitroindandione in 100 ml of ethyl alcohol was added a saturated aqueous solution of 1.4 g of hydrazine hydrochloride. The precipitated hydrazine nitroindandione salt was not separated, but instead the whole flask contents was heated on the water bath for 1 hour. The nitroindandione azine (II), a dark red-brown amorphous substance, was obtained on cooling. For its purification, the azine can be dissolved in hot acetone (approximately 1 g of substance dissolves in 200 ml of acetone) and then precipitated by the addition of petroleum ether to the cooled solution. M.p. 225-230° (with decompn.).

5.300 mg, 5.157 mg sub.: 0.666 ml N_2 (14°, 758 mm). 0.649 ml N_2 (15°, 755 mm). Found %: N 14.90, 14.82. $C_{18}H_{10}O_6N_4$. Calculated %: N 14.81.

The precipitated azine was boiled with water and filtered. To the clear orange-red solution was added a saturated solution of table salt until a permanent cloudiness was obtained. On the following day the orange-red precipitate was filtered and washed with a small amount of extremely dilute sodium chloride solution. M.p. 287-290°.

4.029 mg sub.: 1.243 mg AgCl. 0.6598 g sub.: weight loss on drying at 100-110° 0.0490 g. Found %: Cl 7.64; H_2O 7.43. $C_{18}H_{10}O_6N_4 \cdot NaCl \cdot 2H_2O$. Calculated %: Cl 7.50; H_2O 7.62.

2-Bromo-2-nitro-1,3-indandione azine. a) To a suspension of 1 g of the nitroindandione azine in 50 ml of glacial acetic acid with stirring bromine was added from a dropping funnel until decolorization ceased. The mixture was heated and the precipitate went into solution. Lemon-yellow crystals of the 2-bromo-2-nitro-1,3-indandione azine (IV) gradually deposited from the clear orange-red solution. After recrystallization from bromobenzene, m.p. 218°.

6.043 mg sub.: 0.550 ml N_2 (13°, 733 mm). 0.2620 g sub.: 0.1859 g AgBr. Found %: N 10.48; Br 30.18. $C_{18}H_8O_6N_4Br_2$. Calculated %: N 10.45; Br 29.82.

b) To 1 g of the bromonitroindandione in 5 ml of anhdrous alcohol was added 3 drops of hydrazine hydrate. A vigorous reaction ensued and the bromonitroindandione azine was obtained as a yellow precipitate. After recrystallization from bromobenzene, m.p. 218-219°. The mixed melting point with the compound prepared by method "a" failed to show a depression.

Cleavage of 2-bromo-2-nitro-1,3-indandione azine. A mixture of 0.5 g of the 2-bromo-2-nitro-1,3-indandione azine and 30 ml of xylene was heated under reflux for 1 hour. The precipitate dissolved, giving an orange-red solution. To it was added an equal volume of water and the xylene was steam distilled. The distillate had the acrid odor of bromonitromethane. The liquid remaining in the flask, gave a purplish blue color with glycine (ninhydrin reaction).

SUMMARY

2-Nitro-1,3-indandione with hydrazine salts in aqueous or alcohol solution gives the orange-red azine. Hydroxylamine under the same conditions gives only a yellow oxime, so that this reaction can be used as a color reaction for the detection of hydrazine in the presence of hydroxylamine.

The bromination of 2-nitro-1,3-indandione azine gave the yellow 2-bromo-2-nitro-1,3-indandione azine. The same substance was also obtained by the action of hydrazine on 2-bromo-2-nitro-1,3-indandione.

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REACTION OF BUTYL ALCOHOL WITH CARBON DIOXIDE IN THE PRESENCE OF CHROMIC OXIDE ON ALUMINUM OXIDE

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Carbon dioxide at elevated temperature in the presence of catalysts can behave as a mild oxidizing agent. Thus, in the presence of vanadium pentoxide or its mixture with molybdic anhydride at 400-500° the action of carbon dioxide resulted in the oxidation of anthracene to anthraquinone, of ethylene to formaldehyde, and acetylene to acetaldehyde [1]; inthe presence of metal catalysts (Ag, Cu, or their alloys) methane was oxidized to methyl alcohol and formaldehyde [2].

This type of reaction is related to the conversion of methane under the influence of carbon dioxide, leading to the formation of carbon monoxide and hydrogen [3, 4, 5]: $CH_4 + CO_2 \rightarrow 2CO + 2H_2$. It was shown [6] that in the presence of nickel on aluminum oxide or vanadium pentoxide at 500-650°, carbon dioxide also operates in a similar manner on n-butane: $CH_3CH_2CH_2CH_3 + 3CO_2 \rightarrow 6CO + 3H_2 + CH_4$. It was established [7] that in the contact of a mixture of 1-butene and carbon dioxide with chromium oxide catalysts at 500-650° there occurs dehydrogenation to 1,3-butadiene and conversion of the butene: $C_4H_8 + 4CO_2 \rightarrow 8CO + 4H_2$, and also the reduction of carbon dioxide by hydrogen: $CO_2 + H_2 \rightarrow CO + H_2O$.

In the detailed study of the oxidation of alcohols by carbon dioxide in the presence of oxide catalysts at 350-600° it was shown that for isoamyl alcohol the principal course of the reaction was one of oxidation to isovaleraldehyde and isovaleric acid [8, 9, 10]:

$$1)\ RCH_2OH + CO_2 \rightarrow RCHO + HCOOH;$$

$$2)\ RCHO \xrightarrow{HOH} \left[RCH(OH)_2\right] \xrightarrow{CO_2} RCOOH + HCOOH; \quad 3)\ HCOOH \rightarrow CO_2 + H_2.$$

In the present work, we studied the reaction of n-butyl alcohol with carbon dioxide in the presence of chromic oxide on aluminum oxide at 500°. The main reaction product proved to be a mixture of 1-butene and 2-butene (7:3), the yield of which was 40%. A small amount (~1%) of 1,3-butadiene was detected, and also some ethylene and propylene (~5%). The liquid catalyzate contained unsaturated acyclic hydrocarbons with 5, 6, 7, 8 and 9 carbon atoms, of both the ethylene and diene type, the latter containing conjugated double bond systems, and also benzene, toluene, ethylbenzene and xylene. The isomeric pentenes were present in the greatest amount (~40% of the total amount of liquid hydrocarbon mixture).

An increase in the length of the 4-carbon chain proceeded on the basis of the carbon dioxide, 72% of which underwent reaction, in which connection an extremely small amount of carbon monoxide was formed. This process is reminiscent of the hydrocondensation of olefins with carbon monoxide, realized by Ya. T. Eidus, N. D. Zelinsky and K. V. Puzitsky [11, 12, 13], and consisting in the successive lengthening of the olefin molecule by the free methylene radicals, formed from the carbon monoxide and hydrogen present in the reaction mixture.

The starting link in our process is the 1-butene molecule at the moment of its formation in the dehydration of butyl alcohol. Parallel with this, the alcohol is dehydrogenated to butyraldehyde and the carbon dioxide is reduced by hydrogen to carbon monoxide and then to the methylene radical. The latter effects an increase in the length of the carbon chain of the butene molecule, then of the resulting pentene, etc..

$$CH_3CH_2CH_2CHO \xleftarrow{+H_2} CH_3CH_2CH_2CH_2OH \xrightarrow{-H_2O} CH_3CH_2CH{=}CH_2$$

$$CO_2 + 3H_2 \rightarrow CH_2{<} + 2H_2O$$

$$CH_3CH_2CH{=}CH_2 \xrightarrow{+CH_2<} CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{+CH_2<} CH_3CH_2CH_2CH_2CH{=}CH_2, \text{ etc.}$$

The action of the methylene radicals on 1,3-butadiene, the dehydrogenation product of the butene, also resulted in an increase in the length of the carbon chain with the formation of pentadiene, and then of hexadiene and the

other dienes with a greater number of carbon atoms. The presence in the catalyzate of dienes with a conjugated system of double bonds is linked with the catalytic isomerization of dienes [14], possessing (by the conditions for their formation during hydrocondensation) isolated double bonds:

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{+\,CH_2<} CH_2{=}CH{-}CH_2{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}CH{=}CH{-}CH_3$$

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{+\,2CH_2<} CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \rightarrow \begin{cases} CH_3{-}CH{=}CH{-}CH{=}CH{-}CH_3 \\ CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH_3 \end{cases}$$

The resulting butyraldehyde was then decomposed by the usual scheme: $C_3H_7CHO \rightarrow C_3H_8 + CO$. We will mention that the formation of butyraldehyde from butyl alcohol is associated for the most part with catalytic dehydrogenation, and to a considerably lesser degree with the oxidation by carbon dioxide. In the latter case, in accord with the scheme of A. M. Rubinshtein, the carbon dioxide should be almost completely recovered. This failed to occur in our experiments: only 28% of the carbon dioxide taken for reaction was recovered from the reaction.

The carbon dioxide could have also been transformed as the result of the butene conversion: $C_4H_8 + 4CO_2 \rightarrow$ $\rightarrow 8CO + 4H_2$. The conversion of the butene could have also proceeded under the influence of the water, formed in the dehydration of the alcohol and in the reduction of the carbon dioxide: $C_4H_8 + 4H_2O \rightarrow 4CO + 8H_2$. These two reactions for the butene conversion, and also the dehydrogenation of butyl alcohol to the aldehyde, probably were the principal sources of the hydrogen, which was found in such large amount in the gaseous products of the reaction described by us, and which served to reduce the formed carbon monoxide to methylene radicals, the latter effecting an increase in the length of the carbon chain for the alkenes and alkadienes.

The formation of the aromatic hydrocarbons, found in the catalyzate, is associated with the catalytic aromatization of the alkenes and alkadienes whose chain length was at least six carbon atoms.

When butane and the butenes were passed together with carbon dioxide over the same catalyst at 550-650°, the only reaction products obtained by us were the same as those indicated in the work of A. A. Balandina, N. D. Zelinsky and coworkers [7].

EXPERIMENTAL

Into the reaction tube with an internal diameter of 20 mm was charged 105 g (150 ml) of chromic oxide on aluminum oxide [15]. Two traps, cooled to −45°, were connected to the receiver fitted with a reflux condenser. The butyl alcohol (100.0 g) (1.35 moles) was passed over the catalyst in a stream of carbon dioxide (280 ml/min) at 500° for 2 hours and 20 minutes. The space velocity for adding the alcohol was 0.35 $\frac{\text{ml alcohol}}{\text{ml catalyst/hr}}$. Molal ratio $CO_2{:}C_4H_9OH$ = 1.2:1. The catalyzate in the receiver contained 14.9 g of dark oil and 15.3 g of aqueous layer. The yield of the oil layer was reduced when the reaction temperature was lowered or raised. The titration of 10.0 ml of the aqueous layer required 2.1 ml of 0.1 N NaOH.

1. Gaseous reaction products. The traps contained 38.8 g of reddish mobile liquid. The hydrocarbons, distilling on heating up to + 5°, were passed through wash bottles containing bromine. The obtained mixture of bromides (122.2 g) was dried and distilled in vacuo, where the following fractions were obtained at 60 mm:

1st b.p. 73-80°, n_D^{20} 1.5110, d_4^{20} 1.7569, 3.2 g; 2nd b.p. 80-82°, n_D^{20} 1.5139, d_4^{20} 1.7761, 8.3 g; 3rd b.p. 82-84°, n_D^{20} 1.5163, d_4^{20} 1.7883, 64.5 g; 4th b.p. 84-86°, n_D^{20} 1.5166, d_4^{20} 1.7928, 40.5 g.

The residue from the distillation (5.2 g) crystallized; from it was isolated 3.9 g of 1,2,3,4-tetrabromobutane with m.p. 117.5°; the mixed melting point with known 1,2,3,4-tetrabromobutane remained constant. Literature: m.p. 117° [16].

The constants for the dibromide fraction indicated that a mixture of the 1,2-, and 2,3-dibromobutanes was present.

Literature data for 1,2-dibromobutane: b.p. 165-166° (760 mm), n_D^{20} 1.5144, d_4^{20} 1.7946 [17]; b.p. 86° (60 mm) [18]; 2,3-dibromobutane: b.p. 158-158.5° (760 mm), n_D^{20} 1.5120, d_4^{20} 1.7852 [17]; d,l-form: b.p. 82° (60 mm); meso-form: b.p. 78° (60 mm) [18].

The Raman spectra of the combined dibromide fractions confirmed the fact that this mixture contained the 1,2- and 2,3-dibromobutanes (predominantly the first), and also an extremely small amount of 1,2-dibromopropane. The separate dibromides were characterized by the following Raman spectra lines:

1,2-dibromobutane: 352 (10); 533 (12; w); 643 (100); 805 (40); 1227 (40); 1270 (6; w);

meso-2,3-dibromobutane: 299 (13; w); 603 (4); 633 (60); 843 (8); 1152 (12);

d,l-2,3-dibromobutane: 180 (85); 500 (13); 633 (60); 822 (5); 1209 (10);

1,2-dibromopropane: 299 (13; w); 462 (13); 533 (12; w); 562 (2; b); 643 (100); 843 (8).

As a result, the gases condensed in the traps contained 0.6 g of butadiene, 30.5 g of a mixture of butenes (the yields were respectively ~1% and 40% of theory), and a trace of propylene.

The gases, not condensing in the traps, were passed through wash bottles containing bromine. The obtained dibromides distilled at 57-67° (60 mm), n_D^{20} 1.5222, d_4^{20} 1.9850. Yield, 14.3 g.

Literature data for 1,2-dibromoethane: b.p. 130.5° (758 mm), n_D^{20} 1.53891, d_4^{20} 2.1829 [19]; b.p. 57.9° (60 mm) [18]; for 1,2-dibromopropane: b.p. 141.5° (770 mm), n_D^{20} 1.52006, d_4^{20} 1.9324 [19]; b.p. 66.4° (60 mm) [18].

The Raman spectra for this mixture of dibromides revealed that it contained 1,2-dibromoethane, 1,2-dibromopropane and some 1,2- and 2,3-dibromobutanes. As a result, the gaseous reaction products contained 2-3 g of mixed ethylene and propylene (total yield ~5%). The separate dibromides were characterized by the following spectral lines:

1,2-dibromoethane: 586 (10); 661 (26); 1258 (1);

1,2-dibromopropane: 299 (18); 463 (8); 533 (10; w); 643 (120); 844 (2.5);

1,2-dibromobutane: 348 (12); 533 (10; w); 643 (120); 805 (20); 1227 (40); 1270 (4);

meso-2,3-dibromobutane: 299 (18); 603 (0.5); 633 (50); 844 (2.5); 1153 (10);

d,l-2,3-dibromobutane: 180 (80; w); 496 (10); 633 (50); 822 (1); 1209 (2).

TABLE 1

Compound	Boiling point	n_D^{20}	d_4^{20}
1,2-Dibromopentane [21, 22]	72-74° (15 mm)	1.5088	1.6708
2,3-Dibromopentane [23]	71.1-71.3° (20 mm)	1.5079	1.6789
1,2-Dibromo-2-methylbutane [24]	47.4-48° (8.5-9.0 mm)	1.5088	1.6711
2,3-Dibromo-2-methylbutane [26]	59.5-61° (19 mm)	n_D^{25} 1.5078	d_4^{25} 1.663
3,4-Dibromo-2-methylbutane [26]	61-62° (12 mm)	1.50932	1.6776

TABLE 2

Fraction No.	Boiling point (750 mm)	n_D^{20}	d_4^{20}	Amount (g)	Fraction No.	Boiling point (750 mm)	n_D^{20}	d_4^{20}	Amount (g)
1	34-64°	1.3940	–	2.25	19	125-128	1.4436	0.7820	0.7
2	64-70	1.4013	–	2.65	20	128-131	1.4543	–	0.85
3	70-90.5	1.4374	–	2.9	21	131-133	1.4618	–	1.05
4	90.5-91	1.4062	0.7474	1.35	22	133-134	1.4640	0.7948	1.4
5	91-92	1.4042	0.7405	3.0	23	134-135	1.4647	0.8108	1.15
6	92-93	1.4048	0.7300	1.5	24	135-136	1.4632	0.8170	1.0
7	93-95.5	1.4082	–	1.35	25	136-137	1.4624	–	1.05
8	95.5-99	1.4174	0.7526	0.9	26	137-138	1.4666	0.8220	2.05
9	99-106	1.4372	–	1.1	27	138-140	1.4698	–	1.05
10	106-109	1.4522	0.7893	1.2	28	140-150	1.4708	–	1.3
11	109-111	1.4511	–	0.95	29	150-160	1.4723	–	0.85
12	111-113	1.4422	0.7679	1.05	30	160-170	1.4788	–	0.95
13	113-116	1.4332	–	0.95	31	170-180	1.4832	–	0.65
14	116-118	1.4278	–	1.3	32	180-190	1.4888	–	0.9
15	118-120	1.4269	0.7478	1.65	33	190-200	1.4963	–	0.5
16	120-121	1.4271	0.7652	1.65	34	200-203	1.4689	–	0.8
17	121-123	1.4349	–	0.9		Residue	–	–	1.45
18	123-125	1.4379	–	0.65		Losses	–	–	1.0

In an analogous experiment the gaseous reaction products, not condensing in the traps, were collected in a gasometer over saturated sodium chloride solution. 31645 ml (NTP) of gas: CO_2 31.8%, CO 5.0%, H_2 50.5%, O_2 1.2%, C_nH_{2n} 7.1%, C_nH_{2n+2} 4.6%. As a result, 0.45 mole of carbon dioxide (28% of the introduced amount) failed to react.

2. Liquid reaction products. The liquid reaction products, obtained from four identical experiments, were examined. The residue (20.6 g) after distilling off the condensed gases, and also the dried catalyzates, were fractionated through a long narrow fractionation column. The following fractions were collected:

1st b.p. 20-22° (753 mm), n_D^{15} 1.3692, 3.6 g; 2nd b.p. 22-34°, n_D^{15} 1.3837, 15 g; 3rd b.p. 34-38°, n_D^{15} 1.3883, 4.9 g; 4th b.p. 38-70°, 10.8 g; 5th b.p. 70-160°, 41.9 g; viscous black residue, 5.3 g.

A) The 1st, 2nd and 3rd fractions were mixtures of isomeric pentenes. To 10.0 g of the 2nd fraction in 50 ml of chloroform at −40° was added a chloroform solution of bromine. The obtained dibromides (34.8 g) were distilled in vacuo to give the following fractions (at 15 mm):

B.p. 49-57°, n_D^{20} 1.5137, d_4^{20} 1.6846, 1.2 g; b.p. 57-64°, n_D^{20} 1.5098, d_4^{20} 1.6789, 14.3 g; b.p. 64-70°, n_D^{20} 1.5072, d_4^{20} 1.6755, 11.2 g; b.p. 70-76°, n_D^{20} 1.5080, d_4^{20} 1.6741, 5.9 g; residue, 1.6 g.

Judging from the constants, the collected fractions were mixtures of isomeric bis-dibromopentanes. This was confirmed by the analysis data obtained for two of the fractions (b.p. 57-64° and 64-70°) by the method of A. V. Stepanov [20].

Found %: Br 69.31, 69.49. $C_5H_{10}Br_2$. Calculated %: Br 69.50.

The literature data for the isomeric bis-dibromopentanes are given in Table 1.

TABLE 3

Fraction No.	Boiling point (750 mm)	Amount (g)	Composition of the fractions from the spectroscopic data	Characteristic spectral lines for the quantitative calculation of the fraction compositions
3	70-90.5°	2.9	~40% benzene	606 (5.5); 850 (1.2); 992 (80); 1175 (4.5); 1586 (2.5); 1606 (2)
			~30% conjugated diene	1656 (60); 1668 (20)
			~30% alkene	1643 (26)
			Traces >C=O	1700 (0.5); 1723 (0.5)
4-6	90.5-93	5.8	~35% cis-alkene	1656 (3)
			~65% trans-alkene	1668 (5.5)
10-11	106-111	2.1	~65% toluene	217 (10; w); 522 (7); 786 (20); 1002 (30); 1212 (6); 1605 (3)
			~35% conjugated diene	1654 (100); 1662 (60)
14-16	116-121	4.9	~30% cis-alkene	1655 (5)
			~70% trans-alkene	1670 (12)
21-24	131-136	4.6	~24% ethylbenzene	621 (1); 769 (2.5); 970 (1.5); 1000 (6); 1032 (1.2); 1323 (1)
			~34% p-xylene	307 (3; w); 460 (5); 643 (2); 808 (2); 830 (5); 1620 (1)
			~2% o-xylene	584 (0.6); 735 (1); 1052 (0.5)
			~40% conjugated diene	1654 (100); 1662 (60)
26-27	137-140	3.1	~10% ethylbenzene	622 (0.5); 769 (1.5); 968 (1); 1000 (4); 1032 (1)
			~33% p-xylene	311 (4; w); 460 (5); 645 (3); 808 (2.5); 830 (10); 1202 (2); 1620 (2.5)
			~39% o-xylene	255 (3.5); 505 (1.5); 582 (5); 735 (14); 1056 (4); 1223 (4); 1605 (1.5)
			~10% conjugated diene	1656 (60); 1662 (60)
			Traces >C=O	1720 (0.6)

B) The 5th fraction (b.p. 70-160° at 753 mm) was then redistilled through a column having an efficiency of 25 theoretical plates; the obtained results are given in Table 2. All of the fractions decolorized potassium permanganate solution and bromine water, which indicated the presence of alkenes. Some high and fairly sharp maxima for the refractive indices indicated that the catalyzate also contained aromatic hydrocarbons – products of the catalytic aromatization of the alkenes: the maxima were observed for those fractions whose boiling points corresponded to those of benzene, toluene, ethylbenzene and the xylenes. The Raman spectra of these fractions were studied for the elucidation of their composition. Due to the small amounts of the separate fractions it became necessary to combine them. The results of the spectroscopic investigation are given in Table 3.

The oxidation of the mixture of fractions 10-11 with potassium permanganate in alkaline solution yielded benzoic acid; m.p. 121°. The mixed melting point with known benzoic acid failed to show a depression. A similar oxidation of the mixture of fractions 21-24 gave benzoic acid (m.p. 121°) and terephthalic acid, the latter identified as the dimethyl ester (m.p. 140-141°). The mixed melting points with known benzoic acid and, correspondingly, with known dimethyl p-phthalate failed to show a depression. The oxidation of the mixture of fractions 26-27 gave o-phthalic acid identified as the anhydride (m.p. 130-131°), and the terephthalic acid, identified as the dimethyl ester (140-141°). The mixed melting points with known o-phthalic anhydride and, correspondingly, with known dimethyl p-phthalate failed to show a depression.

In fractions 4-6 and 14-16, which correspond to the minimum refractive indices, only alkenes were found to be present. The mixture of fractions 4-6 should contain heptenes; fractions 14-16 should contain octenes. The refractive indices and densities of these fractions lie close to the values given in the literature for the heptenes and octenes, respectively. In fractions 3, 10-11, 21-24 and 26-27, in addition to aromatic hydrocarbons, the presence of conjugated dienes was revealed; this was responsible for the lower refractive indices and densities possessed by the indicated fractions when compared with the same values for the corresponding aromatic hydrocarbons. Judging from the boiling points, fraction 3 should contain hexadienes, fractions 10-11 should contain heptadienes, and fractions 21-27 should contain the octadienes and nonadienes.

SUMMARY

1. The reaction of n-butyl alcohol with carbon dioxide at 500° in the presence of chromic oxide on aluminum oxide resulted in the formation of unsaturated acyclic hydrocarbons – the alkenes and alkadienes with a conjugated double bond system – containing 5, 6, 7, 8 and 9 carbon atoms, and also benzene, toluene, ethylbenzene and the isomeric xylenes as aromatization products of the unsaturated hydrocarbons with six and more carbon atoms in the straight chain.

2. The formation of the unsaturated acyclic C_5, C_6, C_7, C_8 and C_9 hydrocarbons is explained by an increase in the length of the butene (formed in the dehydration of n-butyl alcohol) carbon chain, and also of butadiene (formed as the result of butene dehydrogenation), by methylene radicals on the order of the hydrocondensation of alkenes with carbon monoxide in the presence of hydrogen.

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ADDITION OF HYDROGEN HALIDES TO PIPERYLENE AND REACTION OF HALOPENTENES

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The chemical properties of piperylene, being the simplest homolog of divinyl, have as yet been studied to an extremely slight degree. The studies made by A. A. Petrov with coworkers [1] and B. A. Arbuzov with E. G. Kataev [2] revealed that piperylene enters quite readily into different diene synthesis reactions. The reactions for the addition of different halogen derivatives to piperylene have been studied in considerably less detail. In the literature, essentially there exist data only on the bromination and chlorination of piperylene [3, 4, 5].

We began our study on the addition of different halogen derivatives to piperylene with an investigation of the addition of the hydrogen halides – hydrogen chloride and hydrogen bromide. The addition of hydrogen chloride to piperylene, obtained as a by-product in the production of synthetic rubber, was first made by V. Krauze, A. Kogan and A. Kozlovskaya [5]. However, due to contamination of the piperylene with large quantities of ethylene hydrocarbons, they were unable to isolate the pure addition product (product boiled in the range 80-99°). Improved rectification methods now permit the isolation of high purity piperylene from technical mixtures.

Our method for the addition of hydrogen chloride to piperylene was similar to the one used earlier by one of us and M. M. Frolova [6] for divinyl. 2-Chloro-3-pentene and 2-bromo-3-pentene are obtained in good yields as the result of adding hydrogen halides to piperylene.

$$CH_3CH{=}CHCH{=}CH_2 + HHal \rightarrow CH_3CHHalCH{=}CHCH_3.$$

The presence and position of the double bond in 2-chloro-3-pentene was proved by bromination in chloroform solution and oxidation with potassium permanganate. The presence of acetic acid in the oxidation products was demonstrated.

As was shown in our previous studies [7] and the studies of other investigators [8], the allylic halides, containing primary, as well as secondary halogen atoms, are quite reactive in different substitution reactions. In the case of unsymmetrical compounds such reactions are accompanied by allylic rearrangements.

2-Chloro-3-pentene also enters quite readily into different reactions. We studied the hydrolysis of 2-chloro-3-pentene, and also the action on it of alcoholic caustic, sodioacetoacetic ester, salts of dialkylphosphorous acids and the full esters of phosphorous acids.

The hydrolysis of 2-chloro-3-pentene (I) gave two products – 3-penten-2-ol (II) and the dipentenyl ether (III). Apparently, the latter was formed in the reaction due to interaction of 3-penten-2-ol with still unhydrolyzed 2-chloro-3-pentene.

$$\underset{\text{(I)}}{CH_3CHClCH{=}CHCH_3} + \underset{\text{(II)}}{CH_3CHOHCH{=}CHCH_3} \rightarrow \underset{\text{(III)}}{\begin{matrix} CH_3CHCH{=}CHCH_3 \\ | \\ O \\ | \\ CH_3CHCH{=}CHCH_3 \end{matrix}}$$

From the boiling point, the obtained 3-penten-2-ol is identical with the product obtained earlier by Grignard from crotonaldehyde and methylmagnesium iodide [9].

The action of alcoholic caustic on allylic halides, as was shown earlier by one of us, is extremely specific [10]. In the case of the action of alcoholic caustic on 2-chloro-3-pentene only the simple ethers, the methyl and ethyl ethers of 3-penten-2-ol, were isolated.

Interesting results were obtained when 2-chloro-3-pentene and 2-bromo-3-pentene were reacted with the salts of dialkylphosphorous acids and with triethyl phosphite. In the studies of Pudovik with Arbuzov [11], Frolova [6] and Kovyrzina [12] it was shown that the reaction of salts of dialkylphosphorous and dialkylthiophosphorous acids with

allylic halides leads to the formation of phosphonoallyl compounds and, in some cases, to further addition products with the dialkylphosphorous acids – the saturated diphosphonic derivatives.

The reaction of 2-chloro-3-pentene with the sodium salts of diethylphosphorous and di-n-butylphosphorous acid proceeds normally with the formation of the corresponding esters of isopentenylphosphonic acid:

$$(RO)_2PONa + CH_3CHClCH=CHCH_3 \longrightarrow CH_3CH=CHCH(CH_3)P(=O)(OR)_2$$

The study made by different authors of the reactions of the full esters of phosphorous acid with secondary saturated bromides and chlorides revealed that these reactions proceeded with extreme difficulty. It is indicated by Ford-Moore and Williams [13] that in general such reactions fail to proceed. In 2-chloro-3-pentene we also have a secondary halogen atom, but due to the presence of a double bond in the β,γ-position to it, its lability, when compared with that of the secondary alkyl chlorides and bromides, is considerably higher. Actually, earlier we had been able, although in small yield, to realize reaction between triethyl phosphite and secondary methoxychloropentene; the reaction proceeded with allylic rearrangement [11].

When triethyl phosphite was reacted with 2-chloro-3-pentene and 2-bromo-3-pentene the basic product obtained was diethylphosphorous acid. In the case of the 2-bromo-3-pentene, a small amount of the diethyl ester of ethylphosphonic acid was isolated. Evidently, in these reactions the lability of the halogen atom is still insufficient for the substitution reaction to occur, and basically the reaction proceeds in the direction of hydrogen halide cleavage; here the phosphite ester functions as a base.

$$CH_3CHHalCH=CHCH_3 + P(OC_2H_5)_3 \rightarrow CH_3CH=CHCH=CH_2 + [HP(OC_2H_5)_3]^+Hal^- \rightarrow HOP(OC_2H_5)_2 + C_2H_5Hal$$

Piperylene was not isolated by us. At the experimental temperature (+160°) it probably polymerized: a considerable amount of viscous tar was observed in the residue from the distillation.

Apparently, the normal substitution reaction proceeds only very slightly and then only with 2-bromo-3-pentene. This is confirmed by the formation in the reaction of a small amount of the ethyl ester of ethylphosphonic acid:

$$CH_3CH=CHCH(CH_3)Br + P(OC_2H_5)_3 \rightarrow CH_3CH=CHCH(CH_3)P(=O)(OC_2H_5)_2 + C_2H_5Br \quad (1)$$

$$P(OC_2H_5)_3 \xrightarrow{C_2H_5Br} C_2H_5P(=O)(OC_2H_5)_2. \quad (2)$$

Since the last reaction is catalytic in nature, then the small amount of ethyl bromide formed by equation (1) is sufficient for the isomerization of considerable amounts of the phosphite ester.

EXPERIMENTAL

Addition of hydrogen chloride to piperylene. Into each of two thick-walled flasks was placed 200 g of concentrated hydrochloric acid, hydrogen chloride was passed in with cooling to saturation, and then to each was added 55 g of piperylene. The flasks were shaken at room temperature for several hours. Then the top layer in both flasks was separated, combined, washed with water, dilute soda solution, and again with water; after drying over calcium chloride, the product was distilled through a Widmer column. After several distillations there was obtained 122 g of 2-chloro-3-pentene.

B.p. 96-97°, d_4^{20} 0.9001, n_D^{20} 1.4320, MR_D 30.11; calculated 29.70.

0.1391 g sub.: 0.1904 g AgCl. Found %: Cl 33.87. C_5H_9Cl. Calculated %: Cl 33.97.

Bromination of 2-chloro-3-pentene. To a solution of 11.4 g of 2-chloro-3-pentene in carbon tetrachloride with cooling was gradually added 17.4 g of bromine, also in carbon tetrachloride solution. After standing for a day, the reaction mixture was distilled in vacuo. The yield of 2-chloro-3,4-dibromopentane was 23 g.

B.p. 65.5-66° at 3 mm, d_4^{20} 1.7860, n_D^{20} 1.5288, MR_D 45.66; calculated 45.68.

0.1295 g sub.: 0.2552 g AgCl + 2AgBr. Found %: Cl + 2Br 74.13. $C_5H_9Br_2Cl$. Calculated %: Cl + 2Br 73.91.

Oxidation of 2-chloro-3-pentene with potassium permanganate. Into a flask, containing 400 ml of water and 12 g of 2-chloro-3-pentene, with constant mechanical stirring was gradually added 50 g of powdered potassium permanganate. On conclusion of oxidation, the acetic acid in the distillate was precipitated as silver acetate.

0.5199 g sub.: 0.3367 g Ag. Found %: Ag 64.76. $C_2H_3O_2Ag$. Calculated %: Ag 64.67.

Addition of hydrogen bromide to piperylene. Hydrogen bromide was passed into a cooled solution of 50 g of piperylene in 50 g of glacial acetic acid. On reaching the necessary weight increase and after standing for a day at room temperature, the reaction mixture was treated with water and dilute soda solution. The residue was twice distilled in vacuo at 100 mm to remove hydrogen bromide. Final distillation through a Widmer column gave 23.7 g of 2-bromo-3-pentene.

B.p. 116.5° at 760 mm, d_4^{28} 1.2721, n_D^{28} 1.4685, MR_D 32.55; calculated 32.59.

0.1528 g sub.: 0.1928 g AgBr. Found %: Br 53.69. C_5H_9Br. Calculated %: Br 53.65.

Hydrolysis of 2-chloro-3-pentene with aqueous soda solution. Fifty grams of calcined soda was dissolved with heating in 270 ml of water, and to the obtained solution was added 50 g of the chloride. The reaction mixture was heated on the water bath for 6 hours with constant and vigorous mechanical stirring. Then the reaction mixture was cooled and extracted several times with ether. The ether extract was dried over fused sodium sulfate, the ether distilled off, and the residue fractionated. After several distillations there was obtained 12.8 g of 3-penten-2-ol.

B.p. 120-121.5°, n_D^{28} 1.4273, d_4^{24} 0.8295, MR_D 26.63; calculated 26.35.

In addition, there was obtained 6.1 g of the dipentenyl ether.

B.p. 156-157°, d_4^{20} 0.8053, n_D^{28} 1.4310, MR_D 49.50; calculated 49.08.

0.1277 g sub.: 0.3619 g CO_2; 0.1319 g H_2O. Found %: C 77.29; H 11.46. $C_{10}H_{18}O$. Calculated %: C 77.93; H 11.62.

Action of KOH on 2-chloro-3-pentene in methyl and ethyl alcohols. The reaction mixture, composed of 18 g of potassium hydroxide, 80 g of dry methyl alcohol and 20 g of 2-chloro-3-pentene, was heated under reflux on the water bath for 3 hours. Then it was treated with water and extracted several times with ether. After drying over calcium chloride and distilling off the ether, the residue was distilled through a Widmer column. The yield of 2-penten-3-ol methyl ether was 17 g.

B.p. 88-89° at 760 mm, d_4^{20} 0.7663, n_D^{20} 1.3948, MR_D 31.28; calculated 31.08.

0.1546 g sub.: 0.4067 g CO_2; 0.1698 g H_2O. Found %: C 71.75; H 12.20. $C_6H_{12}O$. Calculated %: C 72.00; H 12.00.

When the reaction was run in similar manner in ethyl alcohol solution there was obtained 12.3 g of 2-penten-3-ol ethyl ether.

B.p. 105-106° at 760 mm, d_4^{20} 0.7909, n_D^{20} 1.4042, MR_D 35.31; calculated 35.70.

0.1248 g sub.: 0.3370 g CO_2; 0.1379 g H_2O. Found %: C 73.64; H 12.28. $C_7H_{14}O$. Calculated %: C 73.23; H 12.39.

Action of sodium diethyl phosphite on 2-chloro-3-pentene. To an ether solution of sodium diethyl phosphite, prepared from 30 g of diethylphosphorous acid and 5 g of sodium, was added 20 g of 2-chloro-3-pentene. The reaction mixture was heated on the water bath for 3 hours. A rapid deposition of sodium chloride was observed. After conclusion of reaction and distilling off the ether, the residue was distilled in vacuo. The yield of 2-diethylphosphono-3-pentene was 15 g.

B.p. 107° at 14 mm, d_4^{20} 1.0010, n_D^{28} 1.4338, MR_D 53.57; calculated 53.62.

0.1518 g sub.: 46.76 ml NaOH (T 0.018006). Found %: P 15.36. $C_9H_{19}O_3P$. Calculated %: P 15.03.

Action of sodium dibutyl phosphite on 2-chloro-3-pentene. To an ether solution of sodium dibutyl phosphite, prepared from 40 g of dibutylphosphorous acid and 5 g of sodium, was added 20 g of the chloropentene. The reaction was run and the reaction mixture treated in the same manner as in the preceding experiment. The yield of 2-dibutylphosphono-3-pentene after distillation was 19.8 g.

B.p. 149° at 10 mm, d_4^{20} 0.9410, n_D^{28} 1.4380, MR_D 73.01; calculated 72.63.

0.1431 g sub.: 33.61 ml NaOH (T 0.018006). Found %: P 11.71. $C_{13}H_{27}O_3P$. Calculated %: P 11.83.

Reaction of 2-chloro-3-pentene with triethyl phosphite. Fourteen grams of triethyl phosphite with 11 g of 2-chloro-3-pentene was heated in a sealed tube at 160° for 16 hours. Pressure was absent when the tube was opened. Distillation in vacuo of the reaction mixture gave 11 g of diethylphosphorous acid with b.p. 73° at 10 mm, n_D^{20} 1.4062, and minute amounts of lower and higher boiling fractions. The residue was a thick viscous mass, which decomposed with further heating.

Reaction of 2-bromo-3-pentene with triethyl phosphite. Fourteen grams of triethyl phosphite was heated with 10 g of 2-bromo-3-pentene in a sealed tube at 160° for 16 hours. After distillation in vacuo there was obtained 9.6 g of diethylphosphorous acid with b.p. 74-75° at 13 mm, n_D^{20} 1.4090, d_4^{20} 1.0713. Diethylphosphorous acid reacts violently with metallic sodium. From the higher boiling fraction there was isolated a small amount (~2 g) of the ethyl ester of ethylphosphonic acid with b.p. 84-85° at 13 mm, inert to metallic sodium.

SUMMARY

1. The addition of hydrogen chloride and hydrogen bromide to piperylene was studied. 2-Chloro-3-pentene and 2-bromo-3-pentene were obtained and characterized.

2. The hydrolysis of 2-chloro-3-pentene gave 3-penten-2-ol and the dipentenyl ether; the action of alcoholic alkalies gave the methyl and ethyl ethers of 3-penten-2-ol.

3. The action of sodium diethyl phosphite on 2-chloro-3-pentene gave the corresponding dialkylphosphonopentenes in good yields. The reaction of triethyl phosphite with 2-chloro-3-pentene and 2-bromo-3-pentene leads to the formation of diethylphosphorous acid as the main reaction product.

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*** See Consultants Bureau Translation, page 67.
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REACTION OF DI-p-AMINOPHENYLMERCURY WITH PHENOLS. XI.

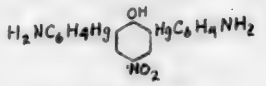
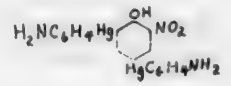
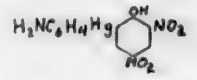
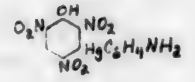
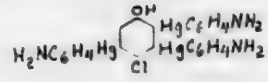
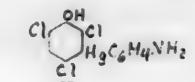
M. M. Koton and V. F. Martynova

In studying the mercuration of phenols with symmetrical aromatic mercury compounds it was shown that the reaction rate depends on the nature of the substituent, found in the benzene nucleus of the organomercury compound [1]. It was interesting to study the mercuration of phenols with di-p-aminophenylmercury, appearing as a highly reactive compound [2]. The reaction was studied with the following phenols: 1) o-nitrophenol, 2) p-nitrophenol, 3) 2,4-dinitrophenol, 4) 2,4,6-trinitrophenol, 5) p-chlorophenol, 6) 2,4-dichlorophenol, 7) 2,4,6-trichlorophenol, 8) p-cresol, 9) resorcinol, and 10) phenol. The reaction was studied in the temperature interval 70-150° in the absence of solvents.

Di-p-aminophenylmercury mercurates the substituted phenols with exceptional ease, already forming at 70° after heating for 3 hours the mono-, di- and trimercury derivatives of the phenols, and aniline:

$$2(H_2NC_6H_4)_2Hg + RC_6H_4OH \rightarrow (H_2NC_6H_4Hg)_2C_6H_2(OH)R + 2C_6H_5NH_2.$$

The presence of the amino group in the benzene nucleus of the organomercury compound gives rise to colored mercury derivatives, which, depending on the phenol, have an orange, green or blue color. Only the derivatives of p-cresol and phenol are colorless. A summary of the obtained compounds is given in the Table.

Names of starting phenols	Formulas of obtained compounds	Structures
p-Nitrophenol	$(H_2NC_6H_4Hg)_2C_6H_2(OH)NO_2$	
o-Nitrophenol	$(H_2NC_6H_4Hg)_2C_6H_2(OH)NO_2$	
2,4-Dinitrophenol	$(H_2NC_6H_4Hg)C_6H_2(OH)(NO_2)_2$	
2,4,6-Trinitrophenol	$(H_2NC_6H_4Hg)C_6H(OH)(NO_2)_3$	
p-Chlorophenol	$(H_2NC_6H_4Hg)C_6H_3(OH)Cl$	—
	$(H_2NC_6H_4Hg)_2C_6H(OH)Cl$	
2,4-Dichlorophenol	$(H_2NC_6H_4Hg)_2C_6H(OH)Cl_2$	—
2,4,6-Trichlorophenol	$(H_2NC_6H_4Hg)C_6H(OH)Cl_3$	
	$(H_2NC_6H_4Hg)_2C_6(OH)Cl_3$	—
Resorcinol	$(H_2NC_6H_4Hg)_2C_6H_2(OH)_2$	—
	$(H_2NC_6H_4Hg)_3C_6H(OH)_2$	—
Phenol	$(H_2NC_6H_4Hg)_3C_6H_2(OH)$	—
p-Cresol	$(H_2NC_6H_4Hg)_3C_6H(OH)CH_3$	—

EXPERIMENTAL

Di-p-aminophenylmercury was prepared according to Chalov [3] by the condensation of p-aminophenylmercury acetate with sodium thiosulfate. Di-p-aminophenylmercury is obtained as white platelets with m.p. 172-174°, difficultly soluble in alcohol, benzene and ether, and soluble in chloroform.

The reaction of di-p-aminophenylmercury with phenols was performed in sealed glass ampoules and was studied at 50, 70, 100, 130 and 150°, with heating for 3, 6 and 9 hours.

For 0.2 g of di-p-aminophenylmercury was taken 0.2 g of the phenols. The reaction products always contained aniline, the presence of which was demonstrated by reaction with benzoyl chloride to give benzoylaniline with m.p. 162° (literature 163°). After removal of the aniline, the reaction mixture was treated with solvents in the following order: aqueous alcohol (1:1), cold alcohol, hot alcohol, benzene, and hot chloroform. The excess phenol was isolated from the aqueous-alcohol extract. The monomercury derivatives were isolated from the alcohol and benzene solutions. The insoluble residue represented the dimercury or trimercury derivatives of the phenols. The separation of metallic mercury was observed in many of the experiments.

I. Di-p-aminophenylmercury and o-nitrophenol. Heating at 70°, 3 hours. After removal of the aniline and o-nitrophenol, an insoluble residue was obtained as fine bright orange crystals (0.2 g). The substance was infusible at 255° and was insoluble in benzene, acetone and chloroform.

0.0300 g sub.: 1.67 ml 0.1 N NH_4CNS. Found %: Hg 55.33. $C_{18}H_{16}O_3N_3Hg_2$. Calculated %: Hg 55.56.

The formation of the dimercurated product ... also proceeded with longer heating at 100 and 130°, but here a small amount of metallic mercury was also isolated.

Proof of the structure of the o-nitrophenol dimercury derivative. 1) Under the influence of an alcoholic HCl solution, the substance underwent cleavage with the formation of aniline, mercuric chloride and o-nitrophenol. 2) The iodination of the substance with a solution of iodine in saturated potassium iodide gave 4,6-diiodo-2-nitrophenol, which from ether solution was obtained as pale yellow crystals with m.p. 109-110° (literature 110°). As a result, the dimercury derivative of di-p-aminophenylmercury and o-nitrophenol has the structure of 4,6-di-p-aminophenylmercury-2-nitrophenol.

II. Di-p-aminophenylmercury and p-nitrophenol. On heating for 3 hours at 100 and 130° there is observed the formation of an insoluble residue (0.16 g), obtained as fine dark blue crystals and failing to melt up to 280°.

0.0423 g sub.: 2.34 ml 0.1 N NH_4CNS. Found %: Hg 55.32. $C_{18}H_{16}O_3N_3Hg_2$. Calculated %: Hg 55.56.

On raising the temperature to 150° the separation of up to 60% of metallic mercury was observed.

The chlorination of the dimercury derivative with chlorine in ether solution gave fine crystals, which melted at 125-126°, thus indicating the presence of 2,6-dichloro-4-nitrophenol (m.p. 125°). Consequently, the dimercury derivative of p-nitrophenol has the structure of 2,6-di-p-aminophenylmercury-4-nitrophenol.

III. Di-p-aminophenylmercury and 2,4-dinitrophenol. Di-p-aminophenylmercury mercurates the dinitrophenol at 100, 130 and 150° with the formation of only the monomercury derivative, which was isolated from benzene solution as fine bright orange crystals (0.15 g) with m.p. 203-205° (decomposition).

0.0482 g sub.: 2.03 ml 0.1 N NH_4CNS. Found %: Hg 42.11. $C_{12}H_9O_5N_3Hg$. Calculated %: Hg 42.18.

In the experiments with heating for 3 hours at 130 and 150° there was observed the separation of mercury in amounts of 6.27 and 53.47%, respectively.

Proof of the structure of the obtained substance. 1) The substance (0.20 g) was cleaved with an alcoholic HCl solution with cooling to −15°, and from the solution on adding water was isolated p-aminophenylmercury chloride (0.0400 g), melting with decomposition at 200°; the mixed melting point with known pure substance failed to show a depression. 2) The iodination of the given product was made with slight heating and shaking. From the ether extract was isolated a deliquescent reddish-yellow mass, which after recrystallization from alcohol was obtained as bright red prismatic crystals with m.p. 105-106°, which corresponded to 6-iodo-2,4-dinitrophenol (from Heilbron, m.p. 106-107°).

The obtained monomercury derivative is 6-p-aminophenylmercury-2,4-dinitrophenol.

IV. Di-p-aminophenylmercury and 2,4,6-trinitrophenol. The reaction between di-p-aminophenylmercury and 2,4,6-trinitrophenol proceeded with the formation of the monomercury derivative only on heating to 130° for 3 hours. The compound was obtained as fine orange crystals (0.140 g) with m.p. 192-195°.

0.0406 g sub.: 1.56 ml 0.1 N NH_4CNS. Found %: Hg 38.42. $C_{12}H_8O_7N_4Hg$. Calculated %: Hg 38.45.

Consequently, the compound is 3-p-aminophenylmercury-2,4,6-trinitrophenol.

V. Di-p-aminophenylmercury and resorcinol. On heating at 70° for 3 hours there was obtained an insoluble residue – bright green crystals (0.63 g), decomposing above 200°. The substance dissolved in 0.5 N potassium hydroxide solution and precipitated again with carbon dioxide gas. Insoluble in alcohol and benzene.

0.0503 g sub.: 2.897 ml 0.1 N NH_4CNS. Found %: Hg 57.59. $C_{18}H_{16}O_2N_2Hg_2$. Calculated %: Hg 57.85.

At 70° for 9 hours, after removal of the aniline and resorcinol from the ampoule in the usual manner, there was obtained an insoluble residue (0.14 g) of fine dark green crystals, not melting up to 260°. Insoluble in organic solvents.

0.1030 g sub.: 6.21 ml 0.1 N NH_4CNS. Found %: Hg 60.23. $C_{24}H_{21}O_2N_3Hg_3$. Calculated %: Hg 61.07.

The presence of mercurated products in the reaction mass could not be detected when the temperature was raised to 130°. Thus, on heating for 9 hours there was found 90.06% of metallic mercury. Consequently, di-p-aminophenylmercury mercurates resorcinol with the formation of the dimercury product $(p\text{-}H_2NC_6H_4Hg)_2C_6H_2(OH)_2$ and the trimercury product $(p\text{-}H_2NC_6H_4Hg)_3C_6H(OH)_2$.

VI. Di-p-aminophenylmercury and p-chlorophenol. Heating at 70° for 3 hours. Bright yellow crystals (0.1 g) were isolated from alcohol solution, m.p. 180-181°.

0.0500 g sub.: 2.36 ml 0.1 N NH_4CNS. Found %: Hg 47.20. $C_{13}H_{10}ONClHg$. Calculated %: Hg 47.75.

An insoluble residue was obtained as fine dark green crystals (0.12 g), not melting up to 260°.

0.0562 g sub.: 3.38 ml 0.1 N NH_4CNS. Found %: Hg 60.10. $C_{24}H_{20}ON_3ClHg_3$. Calculated %: Hg 59.95.

Chlorination of the substance in ether solution gave slender needles of 2,3,4,6-tetrachlorophenol with m.p. 68°. After recrystallization from ligroin m.p. 70°; the mixed melting point remained constant. Consequently, the dark green crystals are 2,3,6-tri-p-aminophenylmercury-4-chlorophenol.

VII. Di-p-aminophenylmercury and 2,4-dichlorophenol. Experiments were made at 50, 70, 100 and 130°. The principal reaction product was a dark green crystalline substance, not melting up to 260°, and sbluble in alkalies.

0.0536 g sub.: 2.84 ml 0.1 N NH_4CNS. Found %: Hg 53.00. $C_{18}H_{14}ON_2Cl_2Hg_2$. Calculated %: Hg 53.74.

VIII. Di-p-aminophenylmercury and 2,4,6-trichlorophenol. In the experiments with heating at 70 and 100° for 3 hours, there was isolated from alcohol a green crystalline substance with m.p. 195-197°.

0.0502 g sub.: 2.021 ml 0.1 N NH_4CNS. Calculated %: Hg 40.25. $C_{12}H_8ONCl_3Hg$. Calculated %: Hg 40.77.

The insoluble residue was a dark blue, infusible, crystalline substance.

0.0524 g sub.: 2.67 ml 0.1 N NH_4CNS. Found %: Hg 51.02. $C_{18}H_{13}ON_2Cl_3Hg_2$. Calculated %: Hg 51.32.

The obtained mercurated products dissolved in different alkalies and were reprecipitated under the influence of 0.1 N acetic acid and carbon dioxide gas. The monomercury compound can be named 3-p-aminophenylmercury-2,4,6-trichlorophenol. The dimercury compound can be named 3,5-di-p-aminophenylmercury-2,4,6-trichlorophenol.

IX. Di-p-aminophenylmercury and p-cresol. Di-p-aminophenylmercury mercurates p-cresol with the formation of the trimercury derivative as a white crystalline substance, insoluble in alcohol, chloroform and benzene, and not melting up to 260°.

0.0300 g sub.: 1.81 ml 0.1 N NH_4CNS. Found %: Hg 60.60. $C_{25}H_{23}ON_3Hg_3$. Calculated %: Hg 61.22.

X. Di-p-aminophenylmercury and phenol. Heating at 70° for 3 hours. After removal of the excess phenol by steam distillation, the residue was treated with alcohol and ether. There was obtained 0.120 g of fine white crystals with m.p. 179°.

0.0550 g sub.: 3.43 ml 0.1 N NH_4CNS. Found %: Hg 62.40. $C_{24}H_{21}ON_3Hg_3$. Calculated %: Hg 62.10.

SUMMARY

It was shown that the mercuration of phenols, possessing different substituents in the benzene ring, by di-p-aminophenylmercury proceeds with great ease, with the formation of colored mono-, di- and trimercury derivatives, and also aniline.

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CONTACT TRANSFORMATION OF CYCLOHEXENE AND 1-METHYL-1-CYCLOHEXENE ON GUMBRIN

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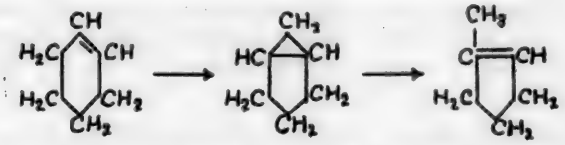
The transformation of cycloolefins in the presence of dehydration contacts, studied in detail by N. D. Zelinsky and Yu. A. Arbuzov [1], as is known, is accompanied by isomerization of the ring, polymerization, and redistribution of hydrogen. The dehydration contacts in the studied investigations were the active aluminum and beryllium oxides [2, 3, 4, 5], kaolin [6], silica gel [7], synthetic aluminosilicates of the cracking type [8-10], and least of all the natural aluminosilicates [11-13].

In the single study, dealing with the transformation of cyclohexene on gumbrin [13], it is indicated that methylcyclopentane, cyclohexane and benzene are formed at 350-400°. The author considered the increase in the refractive index of the catalyzate fraction boiling at 84-86°, and the Raman spectra analysis results obtained for the catalyzate, as evidence for the presence of benzene in the catalyzate. However, in other investigations, dealing with the study of the contact transformations of cyclohexene in the presence of aluminosilicates and active oxides, it was demonstrated that here the formation of benzene fails to occur. A. V. Frost [12] made the postulation that the action of the aluminosilicates on cyclohexene is different from the mechanism of the action of metals, which cause dehydrogenation and irreversible catalysis with the formation of benzene.

Cyclohexene is only isomerized in the presence of aluminosilicates, but not dehydrogenated:



At the same time polymers are formed, which are readily dehydrogenated in the contact with the aluminosilicate and, as a result, are the hydrogen source for the hydrogenation [9].

We set ourselves the task of elucidating the character of the contact transformations of cyclohexene and 1-methyl-1-cyclohexene on gumbrin at a temperature which excluded as much as possible the thermal cracking processes, much coke formation, and changes in the formed cyclohexane [17]. At 320° the transformation of cycloolefins is not accompanied by the separation of considerable amounts of gaseous products, which is usually observed at higher temperatures.

With a space velocity of 0.2 ml/1 ml of contact/hr, the degree of cyclohexene transformation in one pass is 55-60%. The lower boiling catalyzate fractions are devoid of benzene and consist of the methylcyclopentenes, methylcyclopentane, unreacted cyclohexene, and cyclohexane. The lowest boiling catalyzate fractions contain, apparently, 3-methyl-2-pentene and 3-methylpentane, formed as the result of opening the methylcycloheptene ring. The high boiling fractions, representing about 10% in our experiments, consist of a mixture of alicyclic and aromatic hydrocarbons.

The alicyclic hydrocarbon isolated from the polymeric fraction in its constants lies close to the hydrocarbon isolated by Shchekin [9]. A comparison of the ultraviolet absorption spectra of the aromaticized catalyzate fraction with the absorption spectra of naphthalene, tetralin, diphenyl, and diphenylmethane reveals that the character of the absorption spectra of the aromaticized fraction is reminiscent of the condensed systems and is different from the spectra of the bicyclic systems. It can be assumed that the aromaticized fraction consists of a mixture of dimethylnaphthalenes and dimethylhydronaphthalenes, as had been postulated by Bloch and Thomas [8], and consequently, that dehydropolymerization precedes the stage of methylcyclopentadiene formation [14], the contact transformation of which leads to the formation of the dimethylnaphthalenes and their hydro derivatives [15].

The basic transformation products of 1-methyl-1-cyclohexene are dimethylcyclopentene, ethylcyclopentene, dimethylcyclopentane and ethylcyclopentane, the presence of which was proved by the physical constants of the corresponding catalyzate fraction, previously subjected to hydrogenation or sulfonation. In addition, toluene was determined spectroscopically. The basic reaction is contraction of the ring, which makes the scheme proposed by A. A. Petrov [16] and others unconvincing, in accord with which 1-methyl-1-cyclohexene has (in contrast to cyclohexene) a stable six-membered ring. The higher catalyzate fractions, judging from the ultraviolet absorption maxima and sulfonation results, consist of a mixture of aromatic hydrocarbons (naphthalene derivatives) and the alicyclic hydrocarbon $C_{18}H_{32}$.

The data obtained by us support the mechanism proposed by Yu. A. Arbuzov [17] for the contact isomerization of cycloolefins.

EXPERIMENTAL

1. Transformation of cyclohexene. Cyclohexene: B.p. 82-83° (750 mm), n_D^{20} 1.4459, d_4^{20} 0.8108, MR_D 26.98; calculated 27.24; bromine number 194.3; calculated 195.1. The stream method was used for the contact reaction on granulated (0.4-0.5 mm) gumbrin, previously activated by heating for 4-6 hours at 360-370°, with a space velocity of 0.2 ml/1 ml of contact/hr. The experimental data for the contact transformations of cyclohexene are given in Table 1.

TABLE 1

Properties of Cyclohexene Catalyzate

Expt. No.	Weight of taken cyclohexene (g)	Catalyzate weight (g)	Gas volume (l)	Low boiling portion (b.p. 62-83°)					High boiling portion (b.p. 200-260°)		
				% of catalyzate weight	n_D^{20}	d_4^{20}	bromine number	saturated hydrocarbon (%)	% of catalyzate wt.	n_D^{20}	bromine no.
1	67.2	60.15	0.07	84.2	1.4310	0.7815	162.8	16.5	9.8	1.4949	52.8
2	67.0	61.0	0.05	86	1.4405	0.7901	170.0	12.9	11.5	1.4929	52.1
3	74.5	66.2	0.08	87.2	1.4385	0.7868	168.0	14.0	10.1	1.4933	48.2
4	85	76.3	0.07	86.0	1.4362	0.7922	171.0	12.4	10.0	1.500	39.6

TABLE 2

Distillation Results for the Low Boiling Portion of the Cyclohexene Catalyzate

Expt. No.	Boiling point	Yield* (%)	n_D^{20}	d_4^{20}	Saturated hydrocarbons (%)
1	62-68°	4.3	1.4192	0.7612	10.0
2	68-71	6.5	1.4169	0.7610	51.5
3	71-73	13.5	1.4142	0.7544	76.4
4	73-75	6.6	1.4200	0.7620	55.0
5	75-77	12.7	1.4343	0.7871	10.9
6	77-81	8.7	1.4400	0.8506	9.3
7	81-84	44.0	1.4442	0.8093	3.4

A study of the gaseous products proved inexpedient, due to the extremely small amounts involved. The low boiling catalyzate fractions were combined (263 g) and fractionally distilled (Table 2).

Analysis of the low boiling portion of the cyclohexene catalyzate (b.p. 62-84°). Fraction 1, b.p. 62-68°, chiefly consisting of unsaturated hydrocarbons, hydrogenated over Pt. The obtained mixture of saturated hydrocarbons had b.p. 63-72°, n_D^{20} 1.3840, d_4^{20} 0.6920; aniline point +49.5°. Judging from the physical constants, the mixture apparently contains, in addition to methylcyclopentane, an open chain hydrocarbon.

Literature for 3 methylpentane [18]: b.p. 63.28°, n_D^{20} 1.3765, d_4^{20} 0.6643; aniline point 62.5°. For methylcyclopentane: b.p. 71.81°, n_D^{20} 1.4098, d_4^{20} 0.7486; aniline point 34°.

* Based on the total weight of the fractions.

Fraction 2, b.p. 68-71°, consists of a mixture of 1-methyl-3-cyclopentene and methylcyclopentane. Hydrogenation over Pt gave methylcyclopentane; b.p. 72-73°, n_D^{20} 1.4098, d_4^{20} 0.7483, MR_D 27.80; calculated 27.71; aniline point + 35.2°.

Fractions 3 and 4, b.p. 71-75°, combined and hydrogenated over Pt. From its constants the obtained product corresponds to methylcyclopentane: b.p. 71.5-72°, n_D^{20} 1.4093, d_4^{20} 0.7478; aniline point 33.1°.

Fraction 5, b.p. 75-77°, from its physical constants lies close to 1-methyl-1-cyclopentene. The spectroscopic and formolite tests failed to show the presence of benzene. Hydrogenation gave a mixture of methylcyclopentane and cyclohexane, the constants of the mixture were not changed after treatment with 7% oleum: b.p. 71-79°, n_D^{20} 1.4138, d_4^{20} 0.7632; aniline point + 33°.

Fraction 6, b.p. 77-81°. The spectroscopic and formolite tests failed to show the presence of benzene. Cyclohexane was isolated after treatment with 7% oleum: b.p. 80-81°, n_D^{20} 1.4276, d_4^{20} 0.7780, MR_D 27.75; calculated 27.71; aniline point 30.6°.

Literature for cyclohexane [18]: b.p. 80.75°, n_D^{20} 1.4286, d_4^{20} 0.7786; aniline point 31°.

Fraction 7, b.p. 81-84°, represented unreacted cyclohexene. The spectroscopic and formolite tests failed to show the presence of benzene. Hydrogenation gave only cyclohexane.

Analysis of the high boiling portion of the cyclohexene catalyzate (b.p. 200-253°). After removal of unsaturated hydrocarbons with 85% H_2SO_4 the portion was divided into two fractions:

Fraction 1: b.p. 200-232°, d_4^{20} 0.8930, n_D^{20} 1.4932, n_F^{20} 1.5011, n_C^{20} 1.4898; relative dispersion 22.9; aniline point −1.5°.

The qualitative tests for aromatic hydrocarbons were positive. Ultraviolet absorption maxima: 320, 310, 293, 278, 270, 262, 231 mμ. After removal of the aromatic portion with 7% oleum the alicyclic hydrocarbon was isolated: b.p. 215-220°, d_4^{20} 0.8678, n_D^{20} 1.4699, n_F^{20} 1.4755, n_C^{20} 1.4672, MR_D 53.36; calculated 53.22; relative dispersion 17.7; aniline point + 55°. M 160. $C_{12}H_{22}$. Calculated: M 166.

Fraction 2 contains a considerable amount of aromatic hydrocarbons: b.p. 232-242°, d_4^{20} 0.9096, n_D^{20} 1.5082, n_F^{20} 1.5177, n_C^{20} 1.5043; relative dispersion 26.4; aniline point −4.5°. Degree of sulfonation with oleum 68%. We were unable to isolate an individual aromatic hydrocarbon.

TABLE 3

Distillation Results for the Low Boiling Portion of the 1-Methyl-1-cyclohexene Catalyzate

Fraction No.	Boiling point	Yield (%)	n_D^{20}	d_4^{20}	Saturated hydrocarbons (%)
1	50-77°	5.0	1.4190	0.7456	42.5
2	77-80	2.3	1.4438	0.7992	23.0
3	80-86	8.0	1.4402	0.7975	14.9
4	86-90	2.7	1.4257	0.7724	40.8
5	90-94	2.7	1.4242	0.7699	48.0
6	94-99	3.7	1.4265	0.7759	59.5
7	99-101	8.8	1.4286	0.7796	59.0
8	101-102	14.0	1.4315	0.7816	56.0
9	102-107	45.3	1.4455	0.8016	12.6
10	107-111	3.5	1.4474	0.8033	12.0
	Losses	4.0	—	—	—

II. Transformation of 1-Methyl-1-cyclohexene. The same described conditions were used for both 1-methyl-1-cyclohexene and 1-methyl-1-cyclohexanol, the latter undergoing complete dehydration. With a space velocity of 0.2 ml/ml of contact/hr, there was passed 244 g of 1-methyl-1-cyclohexanol in 6 experiments. The residue (coke) on the catalyst failed to exceed 3%, while the volume of evolved gas was insignificant (ca. 200 ml).

There was obtained 170 g of catalyzate, which was divided into two fractions: a) low boiling, b.p. 50-115° (83%); b) high boiling, b.p. 210-255° (17%). The low boiling portion of the catalyzate was fractionally distilled (Table 3).

Fraction 1, b.p. 50-77°, hydrogenated over Pt. A mixture of hydrocarbons was obtained (n_D^{20} 1.4039; aniline point + 40°), judging from its constants, composed of methylcyclopentane and an open chain hydrocarbon. The mixture was not separated due to the small amount.

Fractions 2 and 3 were combined. Hydrogenation over Pt gave cyclohexane admixed with methylcyclopentane: b.p. 79-81°, n_D^{20} 1.4202, d_4^{20} 0.7663; aniline point + 33.9°.

Fractions 4-8 were combined. The presence of toluene was shown spectroscopically (absorption maxima 269, 263 mμ). After removal of unsaturated hydrocarbons with 85% H_2SO_4 the mixture had: b.p. 97-100°, n_D^{20} 1.4263, d_4^{20} 0.7734; aniline point + 38°.

After treatment with 7% oleum to remove aromatic hydrocarbons the constants were close to the constants for a mixture of ethylcyclopentane and 1,2-dimethylcyclopentane: b.p. 98-101°, n_D^{20} 1.4212, d_4^{20} 0.7669; aniline point + 41.4.

Fractions 9-10 were combined: b.p. 102-111°. The presence of toluene was shown spectroscopically (ultraviolet absorption maxima 269, 265, 262, 257, 250, 247 mμ). Hydrogenation over Pt gave a mixture of ethylcyclopentane and methylcyclopentane: B.p. 101-103°, n_D^{20} 1.4257, d_4^{20} 0.7720, aniline point + 35.5°.

Analysis of the high boiling portion of the 1-methyl-1-cyclohexene catalyzate. The fraction with b.p. 220-250° was isolated, containing up to 60% of aromatic compounds: n_D^{20} 1.5018, d_4^{20} 0.8883. Ultraviolet absorption spectra: 320, 289, 272, 268, 224 mμ. Treatment with 7% oleum gave an alicyclic hydrocarbon: b.p. 238-242°, n_D^{20} 1.4883, d_4^{20} 0.8805; MR_D 63.51; calculated 63.0; aniline point + 47.2°. The aromatic hydrocarbon (n_D^{20} 1.5283) isolated from the sulfonic acid was not characterized due to insufficient material.

SUMMARY

1. Cyclohexene under the influence of gumbrin at 320° is transformed into a mixture of methylcyclopentenes, methylcyclopentane and cyclohexane. Benzene is not formed under these conditions. Apparently, the high boiling (dimeric) catalyzate fractions contain the dimethylnaphthalenes and their hydrogenation products.

2. The contact transformations of 1-methyl-1-cyclohexene under these conditions are accompanied by destructive decomposition, as a result of which cyclohexene and its isomerization products are formed, and also toluene. The high boiling catalyzate fractions contain condensed aromatic hydrocarbons and their hydrogenation products.

3. The main source of hydrogen for the formation of alicyclic hydrocarbons is the hydrogen that is evolved in the dehydrogenation of polymers over gumbrin.

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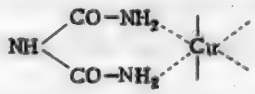
SPECTROPHOTOMETRY OF BIURET COMPLEXES AS A METHOD FOR THE STUDY OF PROTEINS AND PEPTIDES

XVIII. THE BIURET REACTION WITH BRANCHED-CHAIN PEPTIDES

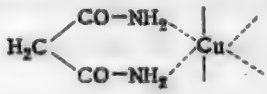
M. I. Plekhan

In previous communications it was shown that the formation of the biuret complex of polypeptides with a long unbroken chain obeys the fundamental rule: every four amino acid radicals combine with one atom of copper, in which connection a red complex is formed.

Chugaev [1] established that a stable biuret complex is formed only under the conditions of creating 5- and 6-membered rings and, consequently, the reaction obeys the Baeyer strain theory. In this way can be explained the fact, for example, that biuret and malonamide form complexes (I) and (II),

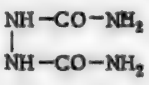


(I)



(II)

while hydrazodicarboxamide (III), succinyldiamide (IV) and succinyldiureide (V) fail to form complexes, since 7- and



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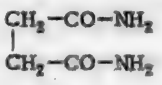

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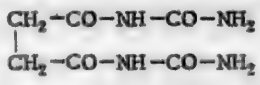
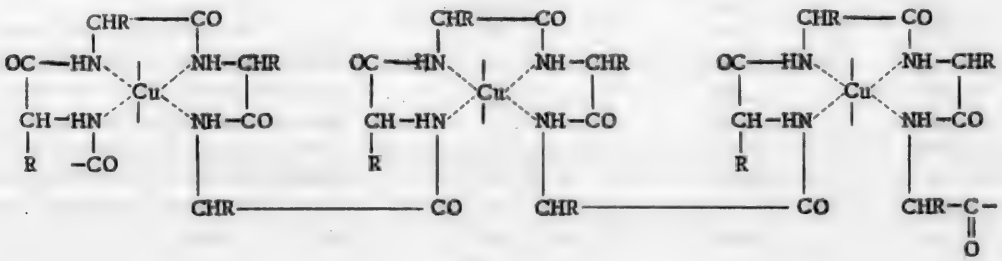


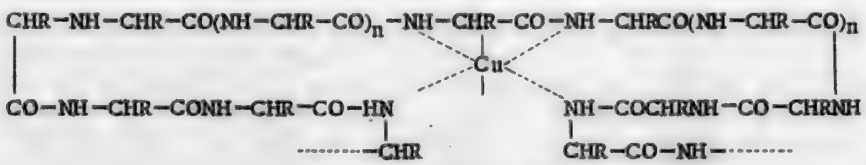
(V)

11-membered rings should have been formed in the last three cases. As a result, if the structural characteristics of the substance are such that higher than 5- and 6-membered rings are formed, then the biuret reaction will prove to be negative. It is specifically for this reason that a polypeptide with a long unbroken chain can form the complex only in accord with Scheme 1



(Scheme 1)

and it is utterly impossible for the complex to be formed in accord with Scheme 2.

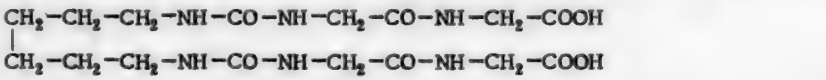


(Scheme 2)

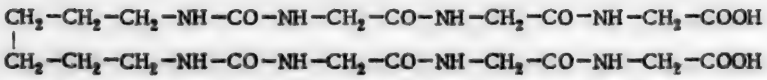
The formation of the biuret complex has hardly been studied for polypeptides with a broken chain. Only one example is known in the literature, which was observed by us together with Gavrilov [2] for synthetic amidine (dihydropyrazinebisglycylglycylglycine). In this compound, containing two tripeptide chains, separated by the

dihydropyrazine ring, the formation of the complex proceeded independently at each chain, and each section of the peptide chain reacted with one atom of copper. We have basis to assume that this is not a solitary phenomenon, but a rule, the confirmation of which on the example of a number of compounds, containing peptide chains broken by different groupings, is of interest, especially in connection with the structure studies of protein substances.

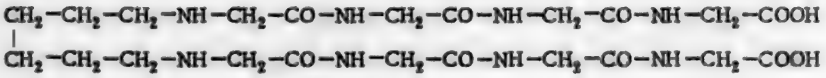
In the present study we investigated the biuret reaction for compounds, in which the peptide chain was broken by the inclusion of a large aliphatic grouping, the hexamethylenebiscarbamoyl radical, and specifically: 1) hexamethylenebiscarbamoylglycylglycine (or hexamethylenebisureidoacetylglycine) (VI), 2) hexamethylenebiscarbamoylglycylglycylglycine (or hexamethylenebisureidoacetylglycylglycine) (VII), and 3) hexamethylenebiscarbamoylglycylglycylglycylglycine (or hexamethylenebisureidoacetylglycylglycylglycine) (VIII):



(VI)



(VII)



(VIII)

TABLE

Optical Densities of Copper Biuret Complexes of Hexamethylenebiscarbamoylpeptides

Wave lengths λ (mμ)	Optical densities ε		
	hexamethylenebiscarbamoylglycylglycine (0.8%)	hexamethylenebiscarbamoylglycylglycylglycine (0.2%)	hexamethylenebiscarbamoylglycylglycylglycylglycine (0.2%)
460	0.051	0.178	0.177
480	0.065	0.279	0.267
500	0.084	0.407	0.395
510	0.096	0.470	0.460
520	0.108	0.525	0.520
530	0.124	0.570	0.565
540	0.140	0.595	0.615
550	0.157	0.602	0.635
555	–	0.598	0.645
560	0.178	0.590	0.640
570	0.193	0.568	0.635
580	0.205	0.535	0.610
600	0.222	0.463	0.550
620	0.231	0.377	0.450
630	0.223	–	–
640	0.216	0.295	0.344
660	0.195	0.215	0.251
680	0.168	0.140	0.166
700	0.142	0.101	0.115
710	0.128	0.084	0.089
730	0.102	0.065	0.058

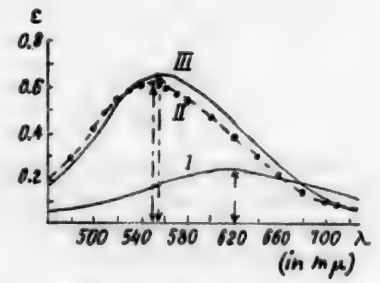
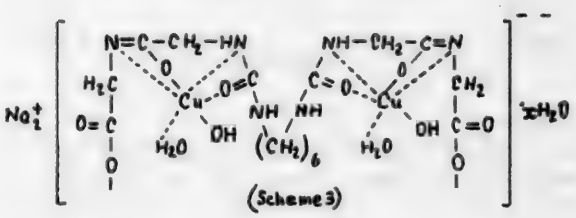


Fig. 1. Spectrophotometric curves for copper biuret complexes of hexamethylenebiscarbamoylpeptide derivatives. I) Hexamethylenebiscarbamoylglycylglycine (0.8% solution); II) hexamethylenebiscarbamoylglycylglycylglycine (0.2% solution); III) hexamethylenebiscarbamoylglycylglycylglycylglycine (0.2% solution).

1. Biuret reaction of hexamethylenebiscarbamoylglycylglycine. The blue biuret complex of hexamethylenebiscarbamoylglycylglycine is formed under the usual reaction conditions for peptides. The iodometric determination for copper revealed that the formation of the complex was extremely slight (8%). This agrees with our observations on the reactions of glycylglycine, where insufficiently active complex formation was noted, and on the reactions of the hexapeptide, in the complex of which the dipeptide remains completely unused.

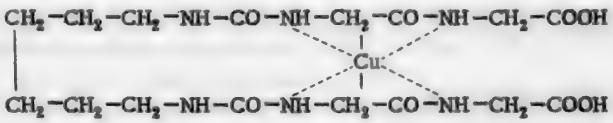
The absorption character (Fig. 1, Table) on the whole lies close to the absorption of the incomplete blue complexes. This means (according to our classification [3]) that only two of the coordinate valences of the copper atom are saturated with the compound containing the nitrogen groups, the other two valences being bound with the oxygen containing groups. Consequently, each copper atom forms an independent portion of the blue complex with the chain segment. We consider the structure of the biuret complex of hexamethylenebiscarbamoylglycylglycine as corresponding to Scheme 3.



(Scheme 3)

Despite the fact that from the total number of nitrogen containing groups it would appear that the given compound should form a red complex, nevertheless the incomplete blue complex is formed. This can be explained in the following manner: the obtained compound in its structure contains the grouping $(CH_2)_6\begin{matrix}NH-CO-NH-\\NH-CO-NH-\end{matrix}$, which represents the amide of the N-substituted carbamic acid (or disubstituted urea). Since the disubstituted ureas fail to give the biuret reaction, then, evidently, in the investigated compound this grouping will also prove to be inactive with respect to complex formation. On the whole, in the biuret reaction the compound behaves like an acylated glycylglycine, in the given case – acylated hexamethylenebiscarbamic acid. The validity of such an explanation is indicated by the shift of the absorption maximum toward the short wave lengths when compared with the glycylglycine complex (620 instead of 670 mμ). We have already observed similar examples of the acylation influence in the case of the carbobenzoxy derivatives of glycylglycine and the alanine dipeptides (racemic and optically active) [4].

It is interesting to note that in the biuret reaction of hexamethylenebiscarbamoylglycylglycine a complex in which both ends of the chain molecule would be bound in accord with Scheme 4 fails to be formed (a red complex would be obtained if the reaction proceeded in this manner).

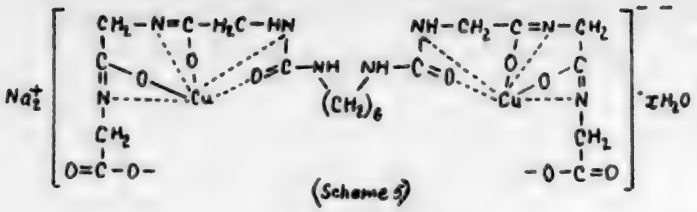


(Scheme 4)

2. The biuret reaction of hexamethylenebiscarbamoylglycylglycylglycine proceeds under the same conditions as for the peptides, in which connection a purple-red color is developed. From the iodometric determination results the complex contains 2 atoms of copper and 1 molecule of the studied substance. The spectrophotometric curve (Fig. 1, Table) has a maximum at a wave length of 550 mμ. This suggests the formation of an incomplete complex in which 3 of the copper coordinate valences are saturated by union with the nitrogen-containing groups, while the fourth valence is saturated by union with the oxygen containing group. It was necessary to exclude mixed complex formation in the given case, i.e., to determine if the red and purple complexes were not simultaneously formed in the molecule of the hexamethylenebiscarbamoylglycylglycylglycine complex.

For this purpose, the copper salt was gradually added to the alkaline solution of the investigated substance and a spectrophotometric analysis made of the obtained colored solution. The results are given in Fig. 2 and in the Table. We see that all of the curves are parallel and have one maximum at wave length 550 mμ. This means that the complex is homogeneous, i.e., the investigated substance forms only one type of complex and in the molecule the two individual portions are structurally analogous. We depict the structure of the hexamethylehebiscarbamoylglycylglycylglycine biuret complex in the following manner (Scheme 5). [See top of following page.]

With respect to complex formation, this compound behaves like the double molecule of glycylglycylglycine, the acylated hexamethylenebiscarbamic acid. This is also indicated by the shift of the absorption maximum toward the short wave lengths (550 instead of the 575 mμ for the free glycylglycylglycine complex). We observed an analogous



(Scheme 5)

acylation influence in the case of the carbobenzoxy derivatives of the glycyl and alanine tripeptides. The molecular absorption intensity for the complex of the investigated substance is 2.5 times greater than for the complex of the free glycylglycylglycine. In this case the hexamethylenebsicarbamic acid radical also fails to participate in complex formation, which is indicated by the position of the maximum. This compound also fails to form a complex in which both ends of the molecule chain would be connected in a manner similar to Scheme 4. Each segment of the peptide chain reacts separately.

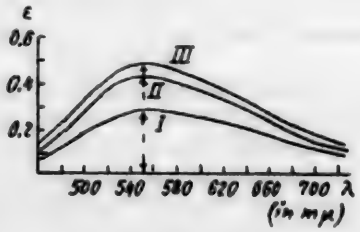


Fig. 2. Study of the homogeneity of the copper biuret complex of hexamethylenebiscarbamoylglycylglycylglycylglycine: 2 ml of 0.77% solution in 4% sodium hydroxide + 2.6 ml of water + n ml of 0.25 M $CuSO_4$ (K = 1.25). I) 0.4 ml $CuSO_4$; ϵ_{max} = 0.276; II) 0.6 ml $CuSO_4$; ϵ_{max} = 0.428; III) 0.8 ml $CuSO_4$; ϵ_{max} = 0.472.

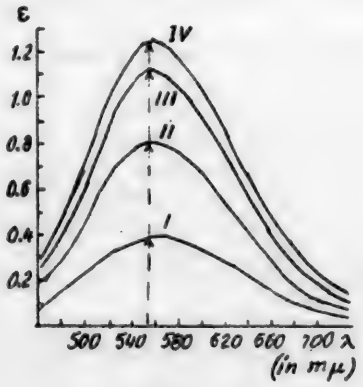
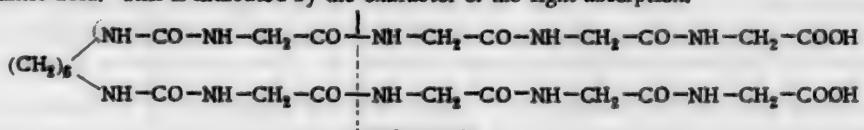


Fig. 3. Study of the homogeneity of the copper biuret complex of hexamethylenebisureidoacetylglycylglycylglycine: 20 mg of substance + 1 ml of 2 N sodium hydroxide + n ml of 0.25 M $CuSO_4$. I) 0.4 ml $CuSO_4$; ϵ_{max} = 0.397; II) 0.8 ml $CuSO_4$; ϵ_{max} = 0.810; III) 1.2 ml $CuSO_4$; ϵ_{max} = 1.13; IV) 1.65 ml $CuSO_4$; ϵ_{max} = 1.230.

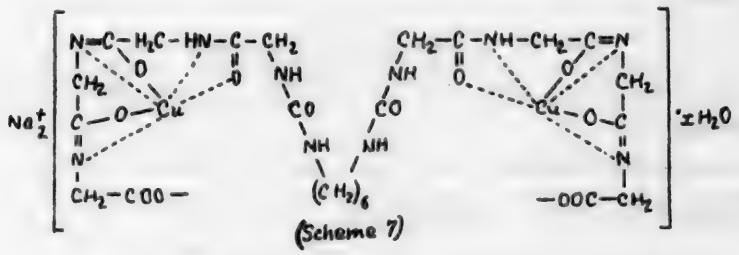
3. Biuret reaction of hexamethylenebiscarbamoylglycylglycylglycylglycine (hexamethylenebisureidoacetylglycylglycylglycylglycine. Hexamethylenebisureidoacetylglycylglycylglycylglycine forms a purple-red biuret complex under the usual conditions. The iodometric determination of copper revealed that the complex contains 2 atoms of copper for 1 molecule of the organic compound. The maximum absorption exists at a wave length of 555 mμ (Fig. 1, Table), which indicates the formation of the incomplete purple complex. The molecular intensity is 3 times greater than for the complex of the free glycylglycylglycine. As indicated above, the homogeneity of the complex was verified. The curves in Fig. 3 are parallelly arranged, and the maximum absorption lies at one wave length of 555 mμ. Consequently, the complex is homogeneous. In particular, the complex in which the copper atom would connect the ends of the molecule chain in a manner similar to Scheme 4, fails to be formed.

With respect to complex formation, the investigated compound behaves like the double molecule of glycylglycylglycine, the acylated hexamethylenebisureidoacetic acid (Scheme 6), and not like the tetrapeptide, the acylated hexamethylenebiscarbamic acid. This is indicated by the character of the light absorption.



(Scheme 6)

The hexamethylenebisureidoacetic acid radical fails to participate in complex formation through its nitrogen containing groups. In this manner is apparently explained the fact that hexamethylenebisureidoacetic acids fails to give the biuret reaction (as had been verified by us on the individual substance). In the investigated compound (hexamethylenebisureidoacetylglycylglycylglycylglycine) the grouping $-NHCH_2CO-$, belonging to the tetrapeptide (in the synthesis of the compound), took part in the formation of the substituted urea derivative; and this fragment of the molecule is not included in the complex formation reaction. In the given case we also observe the phenomenon of selective complex formation since, for example, fragments that are inactive with respect to the biuret reaction can exist in a complex molecule. We depict the structure of the biuret complex of hexamethylenebisureidoacetylglycylglycylglycylglycine by Scheme 7:



(Scheme 7)

The above described investigations of the three compounds revealed the following. Each of the compounds can be considered as a polypeptide, in which the chain is broken by the hexamethylenebiscarbamoyl grouping, which leads to a sharp change in the character of complex formation when compared to the reaction of the peptide with chain intact. The first compound can be considered as being a tetrapeptide, in which the peptide chain is broken; as a result, instead of the red complex, which is characteristic for a tetrapeptide, each segment in the chain (dipeptide) behaves independently and forms a blue complex with a separate copper atom. The second compound can be regarded as being a hexapeptide in which the peptide chain is broken, and instead of the red complex, characteristic for a hexapeptide, each tripeptide segment of the chain separately forms a purple complex. The third compound, hexamethylenebisureidoacetylglycylglycylglycylglycine, can also be regarded as being a hexapeptide with the chain broken by the hexamethylenebisureidoacetyl grouping. In this case also each segment of the peptide chain separately forms a violet complex. In not one of the investigated compounds is a complex with multimembered rings formed.

In all three cases we observe the specific influence of substance structure: it, as it were, is divided with respect to complex formation into functional and nonfunctional fragments. For the broken peptide chain each segment of the chain functions individually. Of especial significance is the fact that even in these complex compounds the properties of the complex (functional fragments) correspond to the properties which we observed for the low molecular peptides and their derivatives.

EXPERIMENTAL

1. Determination of copper in biuret complexes. The substance (40 mg) was dissolved in 2 ml of 2 N sodium hydroxide and 6 ml of water, 2 ml of 0.25 M copper sulfate was added, the excess copper hydroxide was filtered after 1 hour, the colored solution was acidified with acetic acid, and the amount of copper determined iodometrically. In the complex 1 gram-atom of copper is combined with: 326.1 g of hexamethylenebiscarbamoylglycylglycylglycylglycine, 365.1 g of hexamethylenebisureidoacetylglycylglycylglycylglycine. It was found for hexamethylenebiscarbamoylglycylglycine that the reaction was 8% complete.

2. Spectrophotometric analysis of the biuret complexes. Forty milligrams of hexamethylenebiscarbamoylglycylglycine was dissolved in 2 ml of water and 2 ml of 2 N sodium hydroxide, 1 ml of 0.25 M copper sulfate was added, after 10 minutes the solution was filtered (corresponded to an 0.8% solution of the substance) and then analyzed with the aid of a Beckman spectrophotometer. The solutions of the biuret complexes with 0.2% concentrations of hexamethylenebiscarbamoylglycylglycylglycylglycine and hexamethylenebisureidoacetylglycylglycylglycylglycine were prepared in a similar manner.

SUMMARY

1. The biuret complex of hexamethylenebiscarbamoylglycylglycylglycylglycine has an absorption maximum at a wave length of 550 mμ and contains 2 atoms of copper for 1 molecule of organic substance.

2. The biuret complex of hexamethylenebisureidoacetylglycylglycylglycine has a maximum at 555 mμ and contains 2 atoms of copper for 1 molecule of organic substance.

3. The reaction for the formation of the biuret complex of hexamethylenebiscarbamoylglycylglycine proceeds to a very small degree (about 8%), the complex has a maximum at 620 mμ.

4. In the compounds with broken peptide chains each segment of the chain forms a separate complex, the absorption character of which is determined by the number of amino acid radicals in the segment and on the chemical nature of the peptide grouping with which it is associated.

5. In a complex molecule, containing together with the peptide chains other chemical groupings, not complex forming and therefore nonfunctional in this sense, the reaction can proceed on the separate portions – the functional fragments of the molecule.

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First Moscow Medical Institute

* See Consultants Bureau Translation, page 1675.

** See Consultants Bureau Translation, page 531.

REACTION OF ORGANIC BASES WITH METAL SALTS

III. REACTION OF ANTIPYRINE WITH COBALT AND AMMONIUM THIOCYANATES

S. E. Burkat

The present study is a continuation of our investigations in the field of reacting organic bases with the complex thiocyanates of various metals [1, 2]. In the present paper are described the new, as yet not known in the literature, products obtained by us in the reaction of antipyrine with the complex thiocyanate of cobalt and with ammonium thiocyanate.

In accord with the literature, antipyrine forms salts with individual complex acids, which salts are difficultly soluble in water. Thus, antipyrine is readily precipitated in sulfuric acid solution by bismuth iodide in the presence of potassium iodide, and gives a crystalline precipitate with potassium ferrocyanide in acid medium [3]. Gusev [4, 5] developed methods for the qualitative and quantitative determination of cadmium and mercury ions with the aid of antipyrine bromide and antipyrine iodide reagents.

Our experiments revealed that antipyrine and its derivative – pyramidone – give salts with the complex thiocyanates of cobalt, zinc and certain other metals, which salts are difficultly soluble in water, in neutral as well as in acid media. In contrast to pyramidone, which forms characteristic crystalline precipitates with the complex thiocyanates of cobalt and zinc [6, 7], antipyrine gives amorphous masses with the indicated salts.

The addition of a complex cobalt thiocyanate to an acidified solution of antipyrine in water results in the formation of a glasslike substance with a blue color. The qualitative presence of the cobalt ion, the thiocyanate ion and of antipyrine in a saturated water solution of the obtained substance is easily established with the aid of generally accepted reagents.

The formation of the substance can be depicted by the equation

$$4C_{11}H_{12}ON_2 + 2HCl + 4NH_4CNS + Co(NO_3)_2 \cdot 6H_2O = (C_{11}H_{12}ON_2)_2H_2[Co(CNS)_4] \cdot 2C_{11}H_{12}ON_2 + 2NH_4Cl + + 2NH_4NO_3 + 6H_2O.$$

We also studied the behavior of antipyrine and pyramidone toward ammonium thiocyanate; here it was established that pyramidone in neutral and in acid medium fails to give a precipitate with an aqueous solution of ammonium thiocyanate. On the other hand, antipyrine in the presence of dilute mineral acid gives with ammonium thiocyanate solution a white crystalline precipitate. The formation of this substance is all the more of definite interest since antipyrine, under the same experimental conditions, fails to give a precipitate with aqueous solutions of chlorides, bromides and iodides. An aqueous solution of this compound gives the characteristic qualitative tests for antipyrine and thiocyanate ion with the generally accepted reagents. The formation of the obtained compound can be depicted by the equation: $C_{11}H_{12}ON_2 + NH_4CNS + HCl \longrightarrow C_{11}H_{12}ON_2 \cdot HCNS + NH_4Cl$.

EXPERIMENTAL

1. Preparation of antipyrinetetrathiocyanocobaltate. Antipyrine (3.75 g) was dissolved in 50 ml of 0.5 N hydrochloric acid. A solution of 1.45 g of crystalline cobalt nitrate and 5 g of ammonium thiocyanate in 20 ml of water was prepared in a separate vessel. The prepared solution of complex cobalt thiocyanate was added with stirring to the antipyrine solution; here a sky-blue amorphous precipitate was obtained, quickly changing into a tarry viscous mass with a blue color. The obtained product was washed 2-3 times with cold water, then 2-3 times with hot water (70°), and dried at 70°. The yield of substance, based on antipyrine taken for reaction, was 75%.

The glassy blue mass, transparent in a thin layer, is practically insoluble in cold water, slightly soluble in boiling water, and readily soluble in ethyl alcohol. The substance is slightly soluble in dilute mineral acids and in acetic acid, and is soluble in concentrated mineral acids without any characteristic changes. The usual analytical methods were used for the quantitative determination of antipyrine, thiocyanate ion and cobalt in the obtained compound:

Found %: Co 5.29, 5.15; CNS^- 23.21, 23.00; antipyrine 73.00, 72.67. $(C_{11}H_{12}ON_2)_2H_2[Co(CNS)_4] \cdot 2C_{11}H_{12}ON_2$.
Calculated %: Co 5.61; CNS^- 22.40; antipyrine 71.99.

2. Preparation of antipyrine hydrosulfocyanide. Antipyrine (3.75 g) was dissolved in 40 ml of 1 N hydrochloric acid and with vigorous stirring was added 10 ml of a 50% aqueous ammonium thiocyanate solution. The obtained precipitate was filtered, washed on the filter with 10 ml of cold water, and dried at 60°. The yield of technical product was 90%.

The obtained technical product was recrystallized twice from boiling water (first time from 30 ml, the second time from 20 ml) and the crystals dried between filter paper at room temperature. The white crystalline powder is odorless. Under the microscope it consists of colorless needles, slightly soluble in cold water, and readily soluble in hot water, ethyl alcohol and chloroform.

Found %: CNS' 22.98, 23.61; antipyrine 77.52, 76.90. $C_{11}H_{12}ON_2 \cdot HCNS$. Calculated %: CNS' 23.88, antipyrine 76.12.

SUMMARY

The salt of antipyrine with a complex cobalt thiocyanate and the salt of antipyrine with thiocyanic acid were prepared. The composition and some of the properties of the obtained compounds are given.

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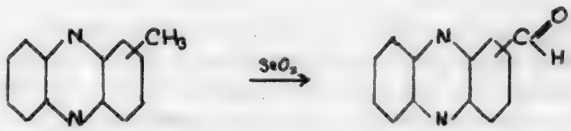
* See Consultants Bureau Translation, page 165.

** See Consultants Bureau Translation, page 1467.

SOME CARBONYL DERIVATIVES OF PHENAZINE

Yu. S. Rozum

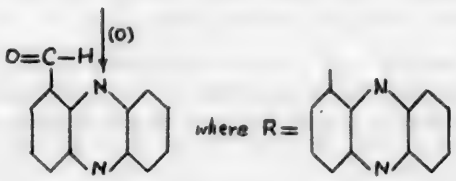
As is known, the thiosemicarbazones of aromatic aldehydes are strongly tuberculostatic [1]. This caused us to synthesize and study the phenazinaldehydes and their thiosemicarbazones. Parallel with this the simpler ketones and quinones of the phenazine series were synthesized. 1-Phenazinealdehyde was first obtained [2] by a complicated and difficult method. The known 1-phenazinealdehyde and the unknown 2-phenazinealdehyde were easily prepared by us in excellent yields from the corresponding 1- and 2-methylphenazines by their oxidation with selenium dioxide:



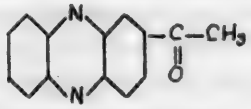
This reaction is both vigorous and rapid, without any side reactions. The obtained aldehydes are characterized as the oximes, phenylhydrazones and thiosemicarbazones, by their condensation reactions with quaternary salts of 2-methylbenzothiazole and α-naphthothiazole, and also by their ultraviolet absorption spectra and polarographic reduction potentials on a dropping mercury electrode. The data obtained by us for the aldehydes and their derivatives are given in the experimental part.

We also obtained 1-phenazinealdehyde by the oxidation of 1-hydroxymethylphenazine with chromic anhydride in acetic acid. The starting 1-hydroxymethylphenazine was obtained from the methyl ester of 1-phenazinecarboxylic acid by reduction with lithium aluminum hydride in absolute ether. The investigated transformations are depicted by the following scheme:

$$2RCOOCH_3 + LiAlH_4 \rightarrow (RCH_2O)_2LiAl(OCH_3)_2 \xrightarrow{4H_2O} 2RCH_2OH + 2CH_3OH + LiOH + Al(OH)_3$$



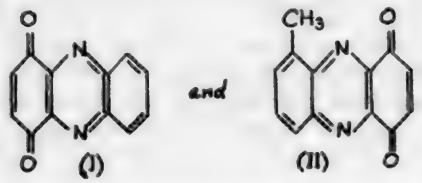
The Grignard reaction with methylmagnesium iodide was run on the obtained 2-phenazinealdehyde. After decomposition of the organomagnesium complex, the obtained secondary methylphenazinylcarbinol was oxidized with chromic anhydride to methyl 2-phenazinyl ketone.



The oxime, 2,4-dinitrophenylhydrazone and thiosemicarbazone were prepared from the methyl 2-phenazinyl ketone. The absorption spectrum of the ketone in the ultraviolet is very close to the spectrum of the phenazine-

aldehyde, while its second stage reduction potential is slightly higher than for the aldehydes. The data for the methyl 2-phenazinyl ketone are given in the experimental part.

The chemical literature on the synthesis of the phenazinequinones is extremely meager. In 1890 Leizester [3] described 6-methyl-5,8-phenazdione as a bronze crystalline powder, which melted at a very high temperature (the melting point was not given). Kehrmann [4] described the synthesis of 2,3-dihydroxy-1,4-phenazdione, which was practically insoluble in all of the organic solvents, but which in alkalies, like all quinones, gave colored solutions. Nietzki and Kehrmann [5] synthesized 2,3-dihydroxy-7-methyl-1,4-phenazdione from rhodizonic acid and 3,4-diaminotoluene. Up to now, the simpler phenazdiones have not been obtained.



We obtained the 1,4-phenazdione (I) and the 1-methyl-5,8-phenazdione (II). At the same time an attempt was made to prepare the 1,5- and 1,7-phenazdiones, but in view of their extreme instability we failed to obtain analytically pure compounds. We attempted to synthesize 1,4-phenazdione by the oxidation of phenazine in a manner analogous to the preparation of 1,4-naphthoquinone [6]. But we had to reject this method, since the phenazine ring proved to be less stable than the naphthalene ring under these conditions; consequently, a second method was chosen, namely, it was decided to convert the corresponding dihydroxyphenazines to the phenazdiones by mild oxidation. Lead tetraacetate (TAL) was used as the oxidizing agent. The phenazdiones obtained by us are colored products, insoluble in the ordinary organic solvents. They dissolve in alkali with a dark yellow, rapidly changing, color. In concentrated hydrochloric acid they dissolve slowly with a purple color. In acid solutions they displace iodine from potassium iodide. On reduction with zinc dust in acetic acid they are transformed into the corresponding hydroxyphenazines. 1,4-Phenazdione and its methyl homolog, similar to benzoquinone and 1,4-naphthoquinone, when treated with acetic anhydride in the presence of sulfuric acid [7] are transformed into 1,2,4-triacetoxyphenazines.

EXPERIMENTAL

2-Methylphenazine was prepared by our improvement of the Merz method [8]. A mixture of 31 g of catechol and 35 g of 3,4-diaminotoluene, thoroughly ground in a mortar, was heated in sealed tubes for 50 hours at 200-220°. The tube contents were washed twice with 100 ml portions of hot water and then dried in the air; here the 2-methyldihydrophenazine was oxidized by atmospheric oxygen to 2-methylphenazine, which was extracted with alcohol and chromatographed on aluminum oxide from ligroin. After two such treatments a product was obtained with m.p. 119° (117° [8]). Yield, 36 g (65%). The maximum yield reached 78%.

1-Methylphenazine was obtained by the alkaline condensation of 32 g of o-toluidine and 50 g of nitrobenzene in the presence of 90 g of powdered potassium hydroxide in 500 ml of boiling toluene. In 10 hours 3.7 ml of water was collected. The product was chromatographically purified on aluminum oxide from ligroin. M.p. 108° (108° [9]). Yield, 6-8%.

1-Phenazinealdehyde. A mixture of 4.2 g of 1-methylphenazine and 4.2 g of freshly distilled selenium dioxide was carefully fused in a wide test tube. A vigorous oxidation began at 150°. Reaction was complete after 5-6 minutes at 160-165°. The aldehyde was extracted from the melt with ether and then recrystallized from methyl alcohol. Yellow needles with m.p. 175°. Yield 3.8 g (80%). Soluble in methyl and ethyl alcohols, acetone, acetic acid, ethylene dichloride and chloroform. Gives red colored solutions in concentrated acids, which are decolorized on dilution with water. Reduction potential 0.31-1.33 V. Ultraviolet absorption maximum 365, 265, 250 mμ. (Found %: N 13.28, 13.25. $C_{13}H_8ON_2$. Calculated %: N 13.46). Thiosemicarbazone – orange needles from alcohol, m.p. 241°. The hydrazone of 1-phenazinealdehyde and isoniazide (hydrazide of isonicotinic acid), pale yellow needles with m.p. 210-211° (from alcohol). Oxime, m.p. 215°.

The boiling for 2 hours of 0.4 g of 1-phenazinealdehyde and 0.6 g of 2-methylbenzothiazole ethiodide in 6 ml of acetic anhydride gave a styryl type dye. After chromatographing on aluminum oxide from chloroform and recrystallization (from a chloroform-ether mixture) there were obtained dark red needles with m.p. 210° (decompn.), yield 9.4%. Absorption maximum in chloroform 547 mμ. In a similar manner, from 2-methylbenzothiazole phenlodide and 1-phenazinealdehyde a product was obtained with m.p. 280° and absorption maximum 555 mμ; fine dark red

prisms, yield 19%. From 2-methyl-α-naphthothiazole ethiodide and phenazinealdehyde a product was obtained with m.p. 267-268°, red needles with a metallic luster, yield 16%. Absorption maximum 575 mμ.

2-Phenazinealdehyde. Obtained in the same manner as the preceding from 6 g of 2-methylphenazine and 6 g of selenium dioxide. Optimum oxidation temperature 180-185°. Yield 6 g (98%). M.p. 185° (from ethyl alcohol). Yellow needles, in clumps. Reduction potential, 0.29-1.29 V. Ultraviolet absorption maximum 365, 265, 252 mμ. Found %: N 13.30, 13.25. $C_{12}H_8ON_2$. Calculated %: N 13.46.

2-Phenazinealdehyde oxime — yellow needles, m.p. 229° (from pyridine). Phenylhydrazone — slender red needles, m.p. 249°. Thiosemicarbazone — orange needles, m.p. 250° (from glycol). Hydrazone of the phenazinealdehyde and isoniazide — yellow needles with m.p. 239°. Hydrazone of 2-phenazinealdehyde and the hydrazide of 1-phenazinecarboxylic acid — light brown needles, m.p. 276° (from glycol). Hydrazone of 2-phenazinealdehyde and 2-benzothiazolylhydrazine — red-brown plates, m.p. 269° (from glycol), gives a blue color in concentrated sulfuric acid.

Methyl 2-phenazinyl ketone. a) Grignard synthesis of the secondary carbinol. The Grignard reagent, prepared from 9 g of methyl iodide and 1 g of magnesium turnings in 150 ml of absolute ether, was added cold to a solution of 4.2 g of 2-phenazinealdehyde in 1.5 liters of anhydrous ether. The mixture was heated with frequent shaking on the water bath for 30 minutes. After 12 hours a solution of 5 g of ammonium chloride in 100 ml of water and 900 g of ice was added. The carbinol went into the ether layer. Yield of crude carbinol 4 g (88%). Yellow plates with m.p. 116° (from methyl alcohol). Readily soluble in acetone and acetic acid, and insoluble in water. Gives a red color in concentrated sulfuric acid.

Found %: N 12.42, 12.38. $C_{14}H_{12}ON_2$. Calculated %: N 12.50.

b) Oxidation of methyl-2-phenazinylcarbinol. A warmed solution of 4 g of the crude carbinol in 15 ml of acetic acid was mixed with a solution of 1.5 g of chromic anhydride in 20 ml of acetic acid. The mixture was cautiously boiled on the gauze for 1 hour; toward the end of boiling about 20 ml of acid was distilled off. The residue was poured into 250 ml of ice water. Yield 2.6 g (65%). Yellowish green plates, m.p. 168° (from alcohol). Gives a red color in sulfuric acid. Soluble in acetone, ethylene dichloride and acetic acid, insoluble in water.

Reduction potential −0.24, −1.40 V. Absorption maximum in alcohol 366, 262 mμ. Found %: N 12.70, 12.48. $C_{14}H_{10}ON_2$. Calculated %: N 12.61.

The 2,4-dinitrophenylhydrazone of the ketone was obtained by boiling for 5 minutes a mixture of 0.22 g of the ketone in 2 ml of acetic acid and 0.2 g of 2,4-dinitrophenylhydrazine in 2 ml of the same solvent. The copious red precipitate obtained on boiling was filtered hot, washed with methyl alcohol and with ether. Yield 0.3 g (75%). Red plates, m.p. 283° (from glycol).

The oxime was obtained by boiling for 30 minutes on the water bath a mixture of 1.12 g of the ketone and 1.5 g of hydroxylamine hydrochloride in the presence of sodium hydroxide. Yield 1 g (84%). M.p. 238° (from pyridine).

The thiosemicarbazone was obtained from 0.22 g of the ketone and 0.13 g of thiosemicarbazide hydrochloride in methyl alcohol by heating on the gauze for 3 hours. Yield 0.2 g (70%). M.p. 266° (yellow needles).

1,4-Phenazdione. To a suspension of 0.21 g of 1,4-dihydroxyphenazine in 5 ml of glacial acetic acid was added in small portions 0.44 g of freshly prepared lead tetraacetate (TAL), and the mixture well-stirred for 15 minutes. After the addition of the first portions of TAL the bright red suspension became colorless, and the temperature rose slightly by 15-20°. The precipitate was filtered, washed with hot acetic acid, methyl alcohol, and ether. Yield 0.16 g (76%). Brown plates with curved ends, m.p. 249-245° (decompn.) (from acetophenone). Difficultly soluble in nitrobenzene and practically insoluble in the ordinary organic solvents. Gives a red color in concentrated sulfuric acid, and a dark purple in hydrochloric acid. Dissolves in alkalies to give a dark yellow solution that rapidly darkens. On reduction with zinc dust in acetic acid it is converted to 1,4-dihydroxyphenazine. The thiosemicarbazone is dark red.

Found %: N 13.37, 13.17. $C_{12}H_6O_2N_2$. Calculated %: N 13.33.

1,2,4-Triacetoxyphenazine. 1,4-Phenazdione (0.1 g) was added to a mixture of 3 ml of acetic anhydride and 3 drops of concentrated sulfuric acid. The reaction product was poured into water. The precipitate was filtered and recrystallized from 60% alcohol. Yield, 0.18 g. M.p. 259-260°. It is slowly saponified on standing in potassium hydroxide or soda and forms a purple-red solution.

Found %: N 7.94, 7.96. $C_{18}H_{14}O_6N_2$. Calculated %: N 7.91.

1,5-Phenazdione. 1,5-Dihydroxyphenazine (0.21 g) was oxidized the same as the preceding with 0.44 g of TAL. Yield 0.2 g. M.p. 308-310° (decompn.) (from acetophenone). Reddish brown plates. Soluble in alkali with

a dark yellow color. Reduction with zinc dust in acetic acid gives 1,5-dihydroxyphenazine. Displaces iodine from potassium iodide in acid solution. Judging from the analysis, the product contained impurities. Repeated recrystallization led to decomposition of the product.

1,7-Dihydroxyphenazine. A mixture of 8.6 g of 1,7-dimethoxyphenazine and 17 g of aluminum chloride was boiled for 20 hours in 400 ml of benzene. The product was purified by a double chromatographing on aluminum oxide from a 1:1 mixture of ethylene dichloride and ligroin, and then was recrystallized from 60% acetic acid. Yield 4.9 g. Yellow needles with m.p. 216°. The compound was analyzed as the diacetyl derivative, which was obtained by boiling 8.5 g of 1,7-dihydroxyphenazine with 50 ml of acetic anhydride for 3 hours. Yield 74%. Yellow needles with m.p. 166° (from alcohol).

1,7-Phenazdione. Obtained in the same manner as the preceding from 0.21 g of 1,7-dihydroxyphenazine and 0.44 g of TAL in glacial acetic acid. Yield 0.2 g. M.p. 305° (decompn.) (from acetophenone). Reduction with zinc dust in acetic acid gives 1,7-dihydroxyphenazine. Displaces iodine from potassium iodide in acid solution. Is changed by repeated recrystallization.

1-Methyl-5,8-dimethoxyphenazine. A mixture of 45 g of 1,4-dimethoxy-2-nitrobenzene, 27 g of o-toluidine and 100 g of potassium hydroxide was boiled in 500 ml of toluene for 9.5 hours. The potassium hydroxide was introduced in two doses to avert violent reaction. The product was precipitated twice from hydrochloric acid solution, extracted with ligroin, and chromatographed on aluminum oxide. Yield 3.4 g (5.4%). Red plates, soluble in benzene, alcohol and ether. Gives a red color in acids. M.p. 189° (from acetic acid).

Found %: N 11.20, 11.12. $C_{15}H_{14}O_2N_2$. Calculated %: N 11.02.

1-Methyl-5,8-dihydroxyphenazine. Obtained by the dealkylation of 5 g of 1-methyl-5,8-dimethoxyphenazine with 12 g of aluminum chloride in 250 ml of boiling benzene for 15 hours. Yield 2.3 g (52%). Red needles, m.p. 174° (from benzene). Gives a blue color in alkalies. Characterized by analysis of the diacetyl derivative, which was obtained from 0.46 g of 1-methyl-5,8-dihydroxyphenazine by boiling in acetic anhydride for 1 hour. Yield 0.01 g. Colorless plates, m.p 160° (from aqueous 60% alcohol).

1-Methyl-5,8-phenazdione. The oxidation of 0.46 g of 1-methyl-5,8-dihydroxyphenazine with 0.88 g of TAL in acetic acid was the same as previously. The end of reaction was determined by the disappearance of color. Yield 0.3 g (68%). Yellow needles, m.p. 290-292° (decompn.) (from butyl alcohol). Displaces iodine from potassium iodide in acid solution, and is reduced by zinc dust in acetic acid to 1-methyl-5,8-dihydroxyphenazine. Gives a red color in alkali, which changes on standing.

Found %: N 12.06, 11.95. $C_{13}H_8O_2N_2$. Calculated %: N 12.50.

1-Methyl-5,7(6),8-triacetoxyphenazine. 1-Methyl-5,8-phenazdione (0.2 g) was added in small portions to a mixture of 5 ml of acetic anhydride and 0.5 ml of sulfuric acid. The product was poured into water. Pale yellow needles, m.p. 205-206° (from aqueous 60% alcohol). Slowly dissolves in alkalies to give dark blue solutions.

Found %: N 7.60, 7.65. $C_{19}H_{16}O_6N_2$. Calculated %: N 7.61.

A SF-4 spectrophotometer was used for measuring the ultraviolet absorption spectra in alcohol solutions at a concentration of 10^{-4} mole/liter. The reduction potentials for the phenazinealdehydes and phenazine ketone were measured on a Model M-8 polarograph of the Gorki Chemical Institute system. 8 in 10^{-3} N ammonium chloride solutions with the addition of 10% of ethyl alcohol at pH 7.00-7.06.

SUMMARY

1. A convenient method for the preparation of 1- and 2-phenazinealdehyde by the oxidation of the 1- and 2-methylphenazines with selenium dioxide was developed.

2. Oxidation of the corresponding dihydroxyphenazines gave the simpler phenazinequinones: 1,4-phenazdione and 1-methyl-5,8-phenazdione.

3. From 2-phenazinealdehyde through the Grignard were obtained the secondary methylphenazinylcarbinol and its oxidation product, the simplest ketone of the phenazine series – methyl 2-phenazinyl ketone.

Derivatives of the discussed compounds were prepared and their properties studied, including measurement of the reduction potentials and ultraviolet absorption spectra.

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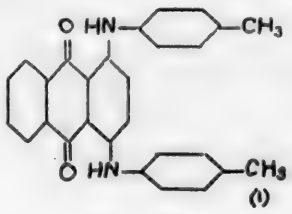
INVESTIGATIONS IN THE POLYCYCLIC QUINONE SERIES

II. 1,4-DIARYLDIAMINOANTHRAQUINONES

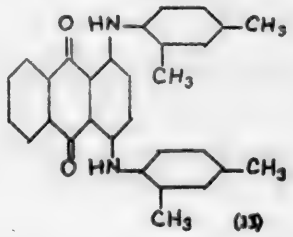
N. S. Dokunikhin and T. N. Kurdyumova

The sulfonic acids of N,N'-diaryl-1,4-diaminoanthraquinone have found extensive use as wool and silk dyes. As a rule, these compounds are colored green. An exception are some patent-described 1,4-diaryldiaminoanthraquinones, which are colored blue, and which contain the mesitylene radical [1], 1,3,5-triethylbenzene [2], durene [3], bromoxylene [4] and certain other compounds. The structural characteristics of these dyes are the presence of substituents in the ortho-positions of the benzene ring connected to the amino group, which should exclude as the result of steric hindrance the possibility of free rotation and arrangement in one plane of the benzene and anthraquinone rings.

In view of the absence in the literature of more detailed information than that which can be gleaned from the patents on the color and structure of compounds of this type, it appeared of interest to make a systemmatic study of the change in the absorption spectra of 1,4-diaryldiaminoanthraquinones as a function of their structure. For this purpose, quinizarin was reacted with the corresponding amines to give the 1,4-di-p-toluidino- (I), 1,4-di-m-xylidino- (II) and 1,4-dimesidinoanthraquinones (III). The bromination of 1,4-di-m-xylidinoanthraquinone gave 1,4-bis-(2',4'-dimethyl-6'-anilino)anthraquinone (IV), the structure of which was proved by reductive cleavage to quinizarin and 6-bromoxylidine. The reaction of 1,4-diaminoanthraquinone with 6-bromo-1,3,5-triethylbenzene was used to obtain 1,4-bis(2',4',6'-triethylanilino)anthraquinone (V).



(I)



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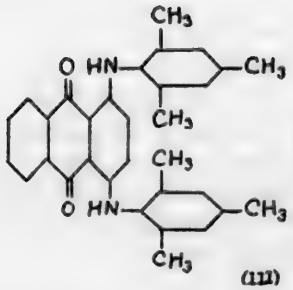

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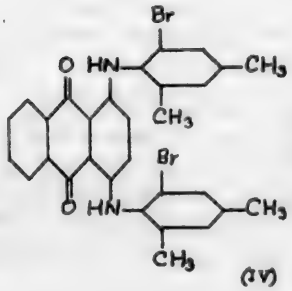

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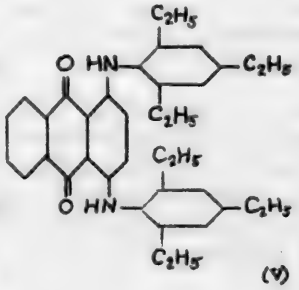
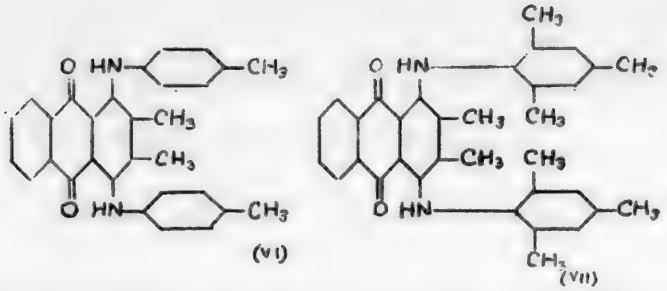


(V)

From our viewpoint, it was of especial interest to study the absorption spectra of 1,4-di-p-toluidino-2,3-dimethylanthraquinone (VI), where the steric hindrance considerations are similar to those for (III). This compound was synthesized by reacting p-toluidine with 1,4-dichloro-2,3-dimethylanthraquinone. The latter was obtained by two methods – the direct chlorination of 2,3-dimethylanthraquinone with sulfuryl chloride [5] and the methylation of the quinizarin leuco compound with formaldehyde [6], followed by replacement of the hydroxyl with chlorine by boiling with thionyl chloride [7]. Also 1,4-dimesidino-2,3-dimethylanthraquinone (VII) was obtained from 1,4-dichloro-2,3-dimethylanthraquinone and mesidine. [See top of following page.]

All of the substances were purified by recrystallization or by chromatographing on aluminum oxide. The light absorption measurements were made in carbon tetrachloride solutions on a SF-4 spectrophotometer. The



(VI) (VII)

measurements were made for two concentrations and showed a satisfactory agreement for the molecular absorption coefficient (Figure and Table).

TABLE

Dye	λ_{max} mμ	$\epsilon \cdot 10^4$	λ_{max} mμ	$\epsilon \cdot 10^4$	λ_{max} mμ	$\epsilon \cdot 10^4$
(I)	645	1.51	610	1.42	410	0.65
(II)	635	1.34	400	0.47	–	–
(III)	630	1.69	485	1.52	–	–
(IV)	620	1.44	575	1.40	–	–
(V)	630	1.85	585	1.60	–	–
(VI)	610	0.88	440	0.45	–	–
(VII)	655	1.41	620	1.32	420	0.48

It was established that in 1,4-diaryldiaminoanthraquinones, in which the ortho-positions in the benzene rings (III), (IV) and (V) are completely substituted, absorption is absent in the short wave length portion of the visible spectrum and the ground maximum is shifted to shorter wave lengths. Substitution of methyl groups in the 2,3-positions of the anthraquinone nucleus in 1,4-di-p-toluidinoanthraquinone leads, together with a considerable shift of the absorption maximum to the shofter wave lengths, to a sharp reduction in the molecular absorption, which had already been observed earlier for other classes of dyes in the presence of steric hindrance [8, 9]. However, a reduction in the molecular absorption coefficient is not observed in the case of (III), (IV) and (V). The light absorption curve for 1,4-dimesidino-2,3-dimethylanthraquinone has an unexpected and as yet unexplained character.

Apparently, the reason for the sharp color change of 1,4-diaryldiaminoanthraquinones in the presence of steric factors should be sought for in the disturbance of conjugation between the anthraquinone and benzene nuclei and weakening of the inner hydrogen bond, the effect of which on absorption in the visible portion of the spectrum for anthraquinone derivatives has already been studied [10]. The noncoplanar structure of the mesidine molecule and its lower polarization in relation to aniline is supported by the results of measuring its dipole moments in benzene and in dioxane [11].

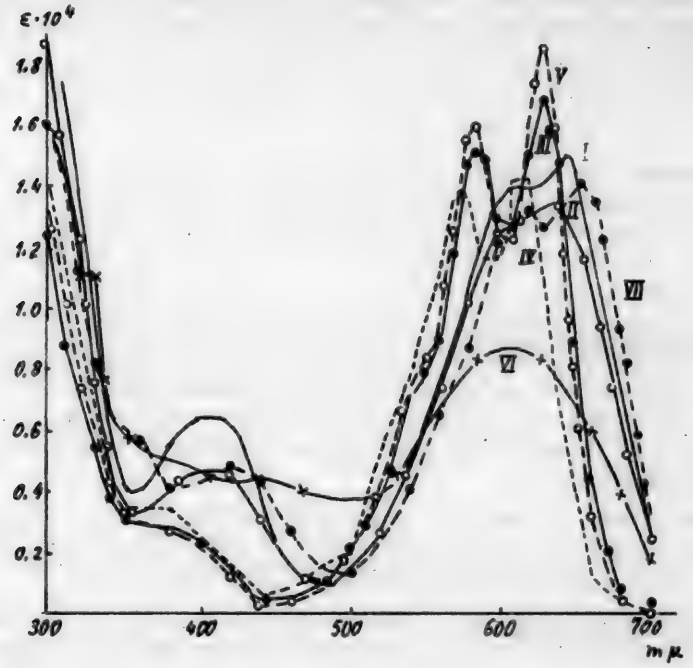
Evidently, the position of the imino hydrogen atom in the plane of the anthraquinone nucleus is determined by the conjugation of the nitrogen atom with the aromatic nucleus, similar to the spatial configuration of the dimethylaniline molecule examined by Kipriyanov [8]. In our examined case the steric hindrance effects produced by the presence of ortho substituents excludes the possibility of forming additional coplanar rings with the hydrogen bond between the imino and carbonyl groups, which in the compound with disturbed conjugation of the benzene and anthraquinone rings should cause a sharp color change in 1,4-diaryldiaminoanthraquinones.

EXPERIMENTAL

1,4-Di-p-toluidinoanthraquinone [12]. A mixture of p-toluidine (51 g), concentrated hydrochloric acid (4.6 g), quinizarin (10.5 g) and boric acid (1.05 g) was heated to 85°, and with good stirring in small portions was added 0.65 g of zinc dust, with simultaneous elevation of the temperature to 95°. The mixture was stirred for 5 hours at this temperature, after which it was cooled to 75°, diluted with methyl alcohol (65 ml), and the obtained crystalline precipitate filtered. Yield 15.8 g. Recrystallized from chlorobenzene.

Found %: C 80.64, 80.72; H 5.29, 5.31; N 6.89, 7.09. $C_{28}H_{22}O_2N_2$. Calculated %: C 80.38; H 5.25; N 6.70.

1,4-Di-m-xylidinoanthraquinone. A mixture of quinizarin (5 g), leucoquinizarin (5 g), glacial acetic acid (10 g), boric acid anhydride (3.4 g), m-xylidine hydrochloride (5 g) and free m-xylidine (45 g) was stirred in a



I) 1,4-Di-p-toluidinoanthraquinone; II) 1,4-di-m-xylidinoanthraquinone; III) 1,4-dimesidinoanthraquinone; IV) 1,4-bis(2',4'-dimethyl-6'-bromoanilino)anthraquinone; V) 1,4-bis(2',4',6'-triethylanilino)anthraquinone; VI) 1,4-di-p-toluidino-2,3-dimethylanthraquinone; VII) 1,4-dimesidino-2,3-dimethylanthraquinone. (In carbon tetrachloride solutions).

stream of nitrogen at 115° for 7-8 hours. After cooling to 70-80°, the mixture was diluted with methyl alcohol (40 ml) and the obtained crystalline precipitate was filtered. Yield 13.25 g (72%). Recrystallized from chlorobenzene.

Found %: C 80.60, 80.70; H 5.80, 5.71; N 6.17, 6.18. $C_{30}H_{28}O_2N_2$. Calculated %: C 80.72; H 5.83; N 6.26.

1,4-Dimesidinoanthraquinone. Obtained from quinizarin (2 g), leucoquinizarin (2 g), glacial acetic acid (4 g), boric acid anhydride (1.36 g), mesidine hydrochloride (2 g), and mesidine (12 g) under the conditions used for the preparation of 1,4-di-m-xylidinoanthraquinone. The substance was isolated by chromatographing a solution of the impure dye in carbon tetrachloride through aluminum oxide. Yield 2.85 g (36%).

Found %: C 80.98, 80.98; H 6.45, 6.49; N 6.03, 6.30. $C_{32}H_{32}O_2N_2$. Calculated %: C 81.01; H 6.33; N 5.90.

1,4-Bis(2'-bromo-4',6'-dimethylanilino)anthraquinone. Bromine (20 g) was added at room temperature and with good stirring to a mixture of 1,4-di-m-xylidinoanthraquinone (22.25 g) with chloroform (190 ml). The reaction mixture was heated on the water bath for 30 minutes to 60° and was then stirred for 1 hour at this temperature. Hydrogen bromide was vigorously evolved. On conclusion of reaction the mass was diluted with methyl alcohol (500 ml), and the obtained precipitate was filtered and washed with alcohol and water. Yield of the bromo derivative 27.7 g (91.7%).

Found %: N 4.40, 4.29; Br 26.83, 26.96. $C_{36}H_{34}O_2N_2Br_2$. Calculated %: N 4.65; Br 26.47.

1,4-Bis(2',4',6'-triethylanilino)anthraquinone. A mixture of 1,4-diaminoanthraquinone (4 g), 1-bromo-2,4,6-triethylbenzene (12 g), nitrobenzene (10 g), calcined soda (2.5 g) and cuprous chloride (0.05 g) was stirred for 6 hours at 180-190°. The cooled reaction mass was diluted with methyl alcohol (50 ml), and the obtained precipitate was filtered and washed with alcohol and water. Yield 7.1 g (76%). The substance is purified by recrystallization from chlorobenzene and by chromatographing in carbon tetrachloride solution on aluminum oxide.

Found %: C 81.97, 82.00; H 7.77, 7.88; N 4.88, 4.66. $C_{38}H_{42}O_2N_2$. Calculated %: C 81.72; H 7.53; N 5.02.

1,4-Dichloro-2,3-dimethylanthraquinone [5, 7]. a) A mixture of 2,3-dimethylanthraquinone with m.p. 206-210° (14.2 g), nitrobenzene (45 g), sulfuryl chloride (13 ml) and metallic iodine (1.5 g) was stirred under reflux for

12 hours at 90-95°. The reaction was terminated when the precipitate, obtained by diluting a sample of the reaction mixture with alcohol, failed to melt below 232°. The reaction mixture was cooled and the obtained bright yellow crystalline precipitate was filtered, washed with alcohol, and dried. Yield 12.22 g (66.6%). Recrystallized from nitrobenzene. M.p. 234-237°.

Found %: C 62.85, 62.91; H 3.29, 3.40; Cl 23.13, 23.17. $C_{16}H_{10}O_2Cl_2$. Calculated %: C 62.95; H 3.28; Cl 23.28.

b) 2,3-Dimethylquinizarin (12 g), obtained by [6] and purified by recrystallization from chlorobenzene, m.p. 250.5-252°, was boiled under reflux for 10 hours with an excess of thionyl chloride (55 ml). Then most of the thionyl chloride was distilled off, while the residue was poured into glacial acetic acid. The obtained dichloroquinizarin was filtered, washed with glacial acetic acid, and recrystallized 2-3 times from glacial acetic acid. M.p. 232.5-234.5°.

1,4-Di-p-toluidino-2,3-dimethylanthraquinone. To a mixture of p-toluidine (40 g), dry potassium acetate (4 g) and metallic copper powder (0.04 g), heated to 150°, was added in small portions over 1 hour with good stirring 4 g of 1,4-dichloro-2,3-dimethylanthraquinone. Then the reaction mixture was heated to 160° and stirred for 3 hours at 160-170°. The reaction mass, cooled to 70°, was diluted with methyl alcohol (60 ml), the obtained precipitate filtered, and washed with alcohol, dilute hydrochloric acid, and water. Yield 4.36 g (73.5%). Separates as purple prisms from chlorobenzene or glacial acetic acid.

5.426 mg sub.: 15.962 mg CO_2; 2.900 mg H_2O. 4.748 mg sub.: 13.796 mg CO_2; 2.490 mg H_2O. 3.621 mg sub.: 0.211 ml N_2 (25°, 737.6 mm). 3.452 mg sub.: 0.200 ml N_2 (21°, 727 mm). Found %: C 80.25, 80.32; H 5.98, 5.86; N 6.47, 6.43. $C_{30}H_{26}O_2N_2$. Calculated %: C 80.72; H 5.83; N 6.28.

1,4-Dimesidino-2,3-dimethylanthraquinone. To a mixture of mesidine (20 g), dry potassium acetate (2 g) and metallic copper powder (0.04 g) at 150° was added over 1 hour with stirring 2 g of 1,4-dichloro-2,3-dimethylanthraquinone, after which stirring was continued for 3 hours at 150-160° and the product isolated as usual by dilution with alcohol. Yield 1.68 g (51%). The substance was purified by recrystallization from chlorobenzene.

3.730 mg sub.: 0.208 ml N_2 (24.5°, 724.7 mm). 3.880 mg sub.: 0.208 ml N_2 (24°, 725.2 mm). Found %: N 6.10, 5.88. $C_{34}H_{34}O_2N_2$. Calculated %: N 5.58.

SUMMARY

1. The light absorption of 1,4-diaryldiaminoanthraquinone derivatives in the visible portion of the spectrum was measured.

2. A theory was expressed for the reasons involved in the color change of 1,4-diaryldiaminoanthraquinones on introducing substituents, which substituents exclude the possibility of planar configuration of the molecule.

3. 1,4-Di-p-toluidino- and 1,4-dimesidino-2,3-dimethylanthraquinones were synthesized.

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OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

VII. SYNTHESIS AND SOME TRANSFORMATIONS OF SILANOLS

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The further development of the chemistry of vinyl ethers is their preparation on the basis of organosilicon compounds. As was established in our investigations [1-2] the reaction of simple vinyl ethers with the trialkyl(aryl)silanols is analogous to the corresponding reaction for the addition of alcohols [3], resulting in the formation of mixed organosilicon acetals with the following structure:

$$R_3SiOH + CH_2 = CHOR' \longrightarrow CH_3CH\begin{matrix}OR' \\ OSiR_3\end{matrix}$$

where: R and R' = alkyl or aryl.

In the present study, methods are described for the preparation of some trialkylsilanols: trimethyl-, methyldiethyl-, and dimethylethylsilanols. The properties of these silanols were studied and on the basis of their reaction with simple vinyl ethers the reaction for the formation of the corresponding organosilicon acetals was studied. The starting products for the preparation of alkyl(aryl)silanols are the corresponding alkyl(aryl)chlorosilanes. Due to the absence of literature data on the properties and sufficiently suitable methods for the preparation of the dimethylethyl- and methyldiethylchlorosilanes [4] it became necessary to develop methods for their synthesis and to study their properties. The most convenient preparation method proved to be the reaction of the corresponding chlorosilanes with ethylmagnesium bromide. The yield of dimethylethylchlorosilane in this case was 44%, and of methyldiethylchlorosilane was 35% of the theoretical.

The general method for the preparation of trialkyl(triaryl)- or alkylarylsilanols is hydrolysis of the corresponding halogen derivatives with alkalies [5]. However, this method proved hardly suitable for the preparation of the first members of the homologous trialkylsilanol series: trimethyl-, dimethylethyl- and methyldiethylsilanols, due to its resulting in the formation of dimers. The silanols were obtained by ammonolysis of the corresponding chlorides and subsequent hydrolysis of the hexaalkyldisilazines in the presence of mineral acids with yields up to 70% of the theoretical. An analogous method is described in the literature only for the preparation of trimethylsilanol [6, 7].

Trimethyl-, dimethylethyl- and methyldiethylsilanols are colorless liquids with a weak camphorlike odor, and are soluble in alcohols, ether, and in chlorinated and aromatic solvents. On dehydration, which most easily proceeds in the presence of mineral acids, the corresponding disiloxanes are formed:

$$R_3SiOH + HOSiR_3 \longrightarrow R_3Si{-}O{-}SiR_3 + H_2O.$$

The dehydration of the indicated silanols is realized even at room temperature. The organosilicon acetals described by us: isopropyl trimethyl-, isobutyl methyldiethyl-, sec-amyl dimethylethyl- and isopropyl diethylphenylsilyl acetals are colorless liquids with an etherlike odor, soluble in the ordinary solvents, but insoluble in water.

EXPERIMENTAL

1. Preparation of Trimethylsilanol

We prepared trimethylsilanol by the earlier described method [7]. To supplement the latter, it is possible by stirring the reaction mass in our proposed method for the preparation of hexamethyldisilazine to shorten the reaction time to 3-4 hours and increase the yield of trimethylsilanol to 90% of the theoretical, based on hexamethyldisilazine.

2. Preparation of Dimethylethylsilanol [9]

1) Preparation of dimethylethylchlorosilane. In an apparatus, consisting of a three-necked flask, fitted with a mechanical stirrer with mercury seal, thermometer, reflux condenser and dropping funnel was placed 48.6 g of magnesium, 600 ml of anhydrous diethyl ether, and 220 g of ethyl bromide was added dropwise over 3 hours. The reaction temperature was maintained at 15-18°. On conclusion of adding the ethyl bromide the flask was heated to

ether boiling for 1-2 hours. Then to a solution of 258 g of dimethyldichlorosilane (2 moles) (b.p. 69-70° at 751 mm, d_4^{20} 1.060) in 400 ml of anhydrous diethyl ether, placed in the above described apparatus, the obtained ethylmagnesium bromide was added from the dropping funnel in 2 hours. The reaction temperature was maintained at 25-30°; after this the flask was heated for 2 hours with ether boiling and allowed to stand overnight. The obtained precipitate was filtered from the ether solution and washed twice with diethyl ether. From the ether solution after repeated rectification there was obtained 108 g (44%) of dimethylethylchlorosilane.

B.p. 89-90° (751 mm), n_D^{20} 1.4105, d_4^{20} 0.8657, MR_D 34.37; calculated 35.54.

Found %: Cl 28.60, 28.53. $C_4H_{11}SiCl$. Calculated %: Cl 28.98.

Literature data [4]: b.p. 89.5-90.5° (760 mm).

2) Preparation of tetramethyldiethyldisilazine [9]. In a three-necked flask, fitted with a mechanical stirrer with mercury seal, gas outlet tube, thermometer and reflux condenser, connected to a trap immersed in a cooling mixture, was placed 61.5 g (0.5 mole) of dimethylethylchlorosilane in 500 ml of anhydrous diethyl ether. The reaction flask was placed in a water bath with a temperature not exceeding +7°, and into the solution with constant stirring was passed a stream of dry ammonia. On conclusion of reaction the obtained precipitate was filtered and washed twice with diethyl ether. The filtrate and ether extracts were fractionated. After repeated fractionation, there was obtained 31 g (65%) of tetramethyldiethyldisilazine.

B.p. 174-175° (750 mm), n_D^{20} 1.4295, d_4^{20} 0.8014, MR_D 60.86; calculated 60.49.

Found %: C 50.28, 50.35; H 12.06, 12.07; Si 30.00, 29.98; N 7.17, 7.22. $C_8H_{23}NSi_2$. Calculated %: C 50.79; H 12.16; Si 29.62; N 7.40.

Literature data [8]: b.p. 175°, d_4^{20} 0.8079, n_D^{20} 1.4214.

3) Hydrolysis of tetramethyldiethyldisilazine. In a three-necked flask, fitted with mechanical stirrer, reflux condenser and dropping funnel, was placed 30 g (0.43 mole) of tetramethyldiethyldisilazine, 20 ml of water, 200 ml of diethyl ether and 3-4 drops of methyl orange. The reaction flask was placed in a water bath with temperature not above +7°, and from the dropping funnel was added 250 ml of 1 N hydrochloric acid solution. The reaction end was revealed by the change in the color of the methyl orange. The ether layer was separated and dried over potash. As the result of distilling the ether layer there was obtained 24 g (80%) of dimethylethylsilanol.

B.p. 58° (50 mm), n_D^{20} 1.4070, d_4^{20} 0.8332, MR_D 30.87; calculated 30.82.

Found %: C 45.63, 45.46; H 11.50, 11.27; Si 27.19, 27.46. $C_4H_{12}OSi$. Calculated %: C 46.15; H 11.53; Si 26.92.

Dimethylethylsilanol is a clear, colorless liquid with a camphorlike odor. Soluble in ether, hydrocarbons, acetone and ethyl alcohol. On storage, heating or treatment with hydrochloric acid it is easily dehydrated with the formation of tetramethyldiethyldisiloxane.

4. Preparation of tetramethyldiethyldisiloxane. In a flask with reflux condenser was placed 20.8 g (0.2 mole) of dimethylethylsilanol and 2-3 drops of 30% hydrochloric acid. The reaction mixture was heated to boiling for 2 hours, dried over potash, and fractionated. Repeated fractionation gave 17.5 g (92%) of tetramethyldiethyldisiloxane.

B.p. 148° (751 mm), n_D^{20} 1.4014, d_4^{20} 0.7995, MR_D 57.93; calculated 58.18.

Found %: C 49.78, 49.88; H 11.42, 11.61; Si 29.51, 29.30. $C_8H_{22}OSi_2$. Calculated %: C 50.69; H 11.64; Si 29.47.

3. Preparation of Methyldiethylsilanol [9]

1) Methyldiethylchlorosilane was prepared in the apparatus and under the same conditions as were used for the preparation of dimethylethylchlorosilane. Ethylmagnesium bromide, prepared from 48 g of magnesium in 600 ml of diethyl ether and 220 g of ethyl bromide, was added from the dropping funnel over 2 hours to a solution of 147 g (1 mole) of methyltrichlorosilane (b.p. 65° (750 mm) in 400 ml of anhydrous diethyl ether. From the ether solution after repeated rectification there was obtained 46.2 g (34%) of methyldiethylchlorosilane.

B.p. 119-120° (757 mm), n_D^{20} 1.4209, d_4^{20} 0.8975, MR_D 38.71; calculated 39.17.

Found %: Cl 25.70, 25.81. $C_5H_{13}SiCl$. Calculated %: Cl 25.94.

Literature data [4]: b.p. 119-120° (760 mm).

2) Preparation of dimethyltetraethyldisilazine. Prepared in the apparatus and under the conditions used for the preparation of tetramethyldiethyldisilazine. The reaction of 45.5 g of methyldiethylchlorosilane, dissolved in 150 ml of anhydrous diethyl ether, with dry ammonia gave 26 g (70%) of dimethyltetraethyldisilazine.

B.p. 111-112.5° (40 mm), n_D^{20} 1.4423, d_4^{20} 0.8316, MR_D 69.08; calculated 69.75.

Found %: C 55.09, 55.15; H 12.62, 12.67; N 6.31, 6.28; Si 25.60, 25.85. $C_{10}H_{27}NSi_2$. Calculated %: C 55.33; H 12.73; N 6.45; Si 25.81.

3) Hydrolysis of dimethyltetraethyldisilazine was achieved by reacting 21.7 g (0.1 mole) of dimethyltetraethyldisilazine, dissolved in 150 ml of diethyl ether, with an 0.5 N hydrochlotic acid solution in the presence of 3-4 drops of methyl orange and 20 ml of water. From the ether solution after repeated fractionation in vacuo there was obtained 14.6 g (ca. 62%) of methyldiethylsilanol.

B.p. 61-62° (30 mm), n_D^{20} 1.4206, d_4^{20} 0.8458, MR_D 35.35; calculated 35.45.

Found %: C 51.45, 51.39; H 11.98, 12.14; Si 24.31, 24.47. $C_5H_{14}OSi$. Calculated %: C 50.85; H 11.86; Si 23.74.

Methyldiethylsilanol is a clear, colorless liquid with a camphorlike odor. Soluble in ethyl ether, hydrocarbons, acetone, and ethyl alcohol. On storage or heating with hydrochloric acid it is readily dehydrated with the formation of dimethyltetraethyldisiloxane.

4) Preparation of dimethyltetraethyldisiloxane. In a flask, fitted with reflux condenser, was placed 11.8 g (0.1 mole) of methyldiethylsilanol and 1-2 drops of 30% hydrochloric acid. The flask was heated for 2 hours on the air bath to boiling. After drying over potash the dimethyltetraethyldisiloxane was isolated by repeated fractionation.

B.p. 87° (19 mm), n_D^{20} 1.4192, d_4^{20} 0.8242, MR_D 66.91; calculated 67.44.

Found %: C 55.04, 54.81; H 11.79, 11.81; Si 25.65, 25.74. $C_{10}H_{26}OSi_2$. Calculated %: C 54.97; H 12.00; Si 25.71.

4. Synthesis of Isopropyl Trimethylsilyl Acetal [9]

In an ampoule, cooled to −8°, was placed 7.3 g (0.08 mole) of trimethylsilanol (b.p. 98-98.6° (757 mm), n_D^{20} 1.3892, d_4^{20} 0.8139), 9.2 g (0.17 mole) of vinyl isopropyl ether (b.p. 55.0-56.0°, n_D^{20} 1.3862, d_4^{20} 0.7520) and by means of a capillary ~0.003 g of 30% hydrochloric acid. The sealed ampoule was heated in a thermostat at 65° for 15 hours. After treatment of the reaction product with fused potash and repeated fractionation, there was obtained 6.2 g (43.3%) of isopropyl trimethylsilyl acetal.

B.p. 36° (16 mm), n_D^{20} 1.3951, d_4^{20} 0.8266, MR_D 51.03; calculated 51.33.

Found %: C 54.64, 54.36; H 11.59, 11f57; Si 15.77, 15.67. $C_8H_{20}O_2Si$. Calculated %: C 54.50; H 11.43; Si 15.92.

5. Preparation of Isobutyl Methyldiethylsilyl Acetal

Isobutyl methyldiethylsilyl acetal was obtained by the above described method. From 7.5 g (0.075 mole) of vinyl isobutyl ether (b.p. 83°, n_D^{20} 1.3988, d_4^{20} 0.7680) 5.5 g (0.046 mole) of methyldiethylsilanol and about 0.003 g of concentrated hydrochloric acid was obtained 4.4 g (43.1%) of isobutyl methyldiethylsilyl acetal.

B.p. 76-77° (7 mm), n_D^{20} 1.4210, d_4^{20} 0.8374, MR_D 65.86; calculated 65.22.

Found %: C 60.33, 60.32; H 11.89, 12.01; Si 13.50, 13.60. $C_{11}H_{26}O_2Si$. Calculated %: C 60.49; H 11.93; Si 12.86.

6. Preparation of sec-Amyl Dimethylethylsilyl Acetal [9]

By the above described method from 11.5 g (0.1 mole) of vinyl sec-amyl ether (b.p. 106.5°, n_D^{20} 1.4070, d_4^{20} 0.7794), 5.2 g (0.05)mole of dimethylethylsilanol and 0.003 g (about) of 30% hydrochloric acid was obtained 6.0 g (55.1%) of sec-amyl dimethylethylsilyl acetal.

B.p. 65-65.5° (7 mm), n_D^{20} 1.4149, d_4^{20} 0.8427, MR_D 65.07; calculated 65.22.

Found %: C 60.57, 60.48; H 12.10, 12.08; Si 13.16, 12.82. $C_{11}H_{26}O_2Si$. Calculated %: C 60.54; H 11.93; Si 12.84.

7. Synthesis of Isopropyl Diethylphenylsilyl Acetal

A mixture of 9.0 g (0.05 mole) of diethylphenylsilanol (b.p. 105.5-108° (5 mm), n_D^{20} 1.5109, d_4^{20} 0.9904), 8.5 g (0.1 mole) of vinyl isopropyl ether (b.p. 55.0-55.7°, n_D^{20} 1.3835, d_4^{20} 0.7500) and 0.02 ml of concentrated hydrochloric

acid was placed in an ampoule. The ampoule was sealed and heated on the boiling water bath for 2.5 hours. The ampoule was opened on the following day, the contents were dried over potash, and fractionated. After repeated fractionation there was obtained 5.1 g of substance.

B.p. 120-121° (5 mm), n_D^{20} 1.4827, d_4^{20} 0.9477, MR_D 80.24; calculated 80.41.

Found %: C 67.57, 67.75; H 9.54, 9.64; Si 10.96, 10.81. $C_{15}H_{26}O_2Si$. Calculated %: C 67.62; H 9.84; Si 10.53.

According to the analysis data the isolated substance was isopropyl diethylphenylsilyl acetal. The yield was 35.6% of theory, based on diethylphenylsilanol. Isopropyl diethylphenylsilyl acetal is a colorless liquid with a sharp persistent odor, soluble in alcohol, acetone, ether, chlorinated and aromatic hydrocarbons, and insoluble in water.

SUMMARY

1. Methyldiethylsilanol and dimethylethylsilanol were prepared and characterized for the first time.

2. Methyldiethylchlorosilane and dimethylethylchlorosilane, and the corresponding disilazines and disiloxanes, were prepared and characterized.

3. It was established that the obtained silanols could be reacted with simple vinyl ethers to give the following organosilicon acetals: isopropyl trimethylsilyl, isobutyl methyldiethylsilyl, sec-amyl dimethylethylsilyl and isopropyl diethylphenylsilyl acetals.

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CATALYTIC TRANSFORMATIONS OF TERPENES

VI. THE CATALYTIC ISOMERIZATION OF α-PINENE INTO β-PINENE

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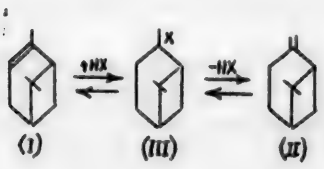
In one of our previous communications [1] it was mentioned that in the incomplete isomerization products of d+α-pinene on titanic acid, obtained at 135-160°, together with tricyclene, camphene, the fenchenes, limonene, terpinolene and the terpinenes, there is present an extremely large amount of an unknown terpene.

It was established in the present study that the above indicated terpene is d-β-pinene. Without doubt, the found d-β-pinene was formed as the result of d-α-pinene isomerization. If β-pinene, present as impurity in the original d-α-pinene, had been found in the reaction products, then levorotatory β-pinene would have been isolated, since only the l-β-pinene is contained in coniferous turpentines, in which connection its optical rotation $[\alpha]_D$ −22.4° is practically constant. The formation of d-β-pinene as the result of d-α-pinene isomerization is also confirmed by the fact that the specific optical rotation of the obtained d-β-pinene $[\alpha]_D$ +10.8° is quite close to the calculated $[\alpha]_D$ + 12.6°.*

The catalytic isomerization of β-pinene into α-pinene under the influence of benzoic acid [4], rosin acids [4] and hydrogen saturated platinum black [5] has been known for a long time. It also proceeds under the influence of titanic acid, together with isomerization into camphene and monocyclic terpenes [6]. The catalytic isomerization of α-pinene into β-pinene is described here for the first time. Since the reaction proceeds with the same catalyst and under the same temperature conditions as the isomerization of β-pinene into α-pinene, and since β-pinene is present only in the incomplete isomerization products of α-pinene, then it must be acknowledged that a reversible equilibrium condition exists between the two pinenes. An approximate calculation reveals that in the equilibrium mixture of the pinenes in the presence of titanium catalyst, there is contained about 98% of α-pinene and about 2% of β-pinene. The presence of equilibrium between α- and β-pinenes is included in the development of the postulations presented in our studies [1, 7, 8]. The intermediate compound (III) formed from either α-pinene (I) or β-pinene (II), on decomposing, can be converted into either α-pinene or into β-pinene.



Since the action of titanic acid on the pinenes is similar to that of a number of other acids and acid catalysts [6-9], then it must be assumed that the described transformation takes place not only when α-pinene is heated with titanic acid, but also when it is heated with many other acids and acid catalysts.

The comparatively easy transition from α-pinene to β-pinene, and the reverse, causes us to ponder on the interrelation of these terpenes in the living tree. If these transformations occurred in nature, then it would seem that β-pinene would fail to have a constant levorotation in d-α-pinene containing turpentines, as is actually the case; consequently, despite the ease of interconversion of these terpenes, the presence of such transformations in the living tree is doubtful, if only for the reason that the optical rotation of l-β-pinene in turpentines actually remains completely constant.

EXPERIMENTAL

The d-α-pinene used by us as starting product was isolated from Pinus sylvestris turpentine, and had the following constants: d_4^{20} 0.8580, n_D^{20} 1.4654, $[\alpha]_D$ +30.3°. The liquid phase isomerization was conducted in the presence of titanic acid catalyst at 160° [1, 8, 9]. The amount of pinene in the obtained isomerizate was 32%. The isomerizate (2500 g) was purified in vacuo using a highly efficient still; here 112 g of a number of fractions was collected, which contained all of the terpene present in the original charge. Of the 112 g of obtained product, 68 g was redistilled.

* Calculated from the proportion $[\alpha]_D = \frac{22.4 \cdot 30}{53}$, where 22.4° = $[\alpha]_D$ of optically pure β-pinene [2], 53° = $[\alpha]_D$ of optically pure α-pinene [3], and 30° = $[\alpha]_D$ of the original α-pinene.

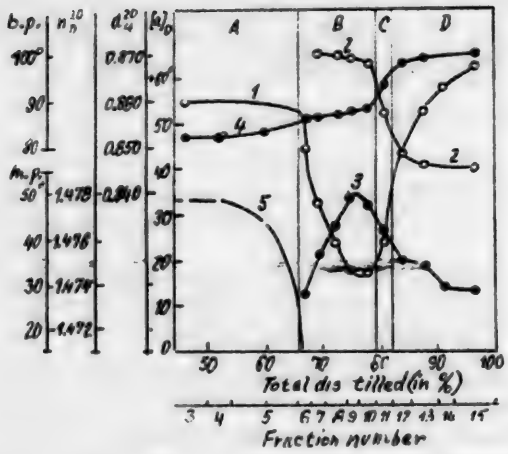


Fig. 1. Isolation of the investigated terpene; final distillation of the narrow isomerizate fraction. 1) $[\alpha]_D$; 2) d_4^{20}; 3) n_D^{20}; 4) boiling point; 5) melting point.

The results of the last distillation are shown in the graph (Fig. 1), and the properties of the more characteristic fractions are given in Table 1; the rotatory dispersion curves for some of these fractions are depicted in Fig. 2.

The collected fractions were divided into four groups, designated on the graph (Fig. 1) by letters from A to D.

Group A (fractions 1-5) consists of camphene. The 3rd fraction contained the purest camphene: M.p. 48°, d_4^{54} 0.8412, n_D^{54} 1.4558. Judging from the melting point, the 5th fraction contains a small amount of the terpene found in group B.

Group B consists of fractions 6-10, containing the investigated terpene and camphene.

Group C consists of the intermediate 11th fraction, containing the investigated terpene, 12.6% of α-terpinene (determined by the diene synthesis reaction method [1]), limonene, and probably a small amount of camphene.

Group D (fractions 12-15) essentially consists of limonene, the amount of which is greatest in the 15th fraction. The 12th fraction contains 12% of α-terpinene and, apparently, also another unidentified optically inactive hydrocarbon. The presence of this hydrocarbon is indicated by the different optical rotation of the 12th and 15th fractions after removal of the α-terpinene ($[\alpha]_D$ +48.9° and +62.3°) from them, with the rotatory dispersion coefficients being the same.

TABLE 1

Properties of Some of the Fractions Obtained in the Isolation of the Investigated Terpene

Fraction No.	Amount of camphene (%)	d_4^{20}	n_D^{20}	$[\alpha]_{656.3}^{20}$	$[\alpha]_{589.3}^{20}$	$[\alpha]_{578.0}^{20}$	$[\alpha]_{546.1}^{20}$	$[\alpha]_{436.1}^{20}$	$[\alpha]_{\ }^{20}$ *
3**	100	—	—	+42.23°	+54.61°	+57.91°	+66.21°	+89.77°	+120.06°
7	50	0.8708	1.4753	+25.73	+32.72	+34.64	+39.15	+51.35	+ 65.28
8	30.2	0.8698	1.4765	+19.13	+24.03	+25.42	+28.45	+35.80	+ 44.15
9	16	0.8680	1.4777	+14.65	+17.79	+18.79	+20.66	+24.98	+ 28.45
10	14.5	0.8670	1.4774	+14.03	+17.18	+17.97	+19.98	+23.97	+ 27.19
15	—	0.8445	1.4734	+47.68	+61.96	+65.13	+73.92	+96.36	+123.66

Based on the course of the curves shown in the graph (Fig. 1) and the physical properties of the group B fractions, it can be assumed that in them, especially in the 6-9th fractions, the monocyclic terpenes are absent, and the indicated fractions can be considered as being binary mixtures of camphene and the investigated terpene.

From the boiling points, d_4^{20} and n_D^{20}, the 9th and 10th fractions, being richest in the investigated terpene, lie close to β-pinene. The sloping rotatory dispersion curve (Fig. 2) also indicates the presence of β-pinene in these fractions.

One of the most characteristic properties of β-pinene is its anomalous rotatory dispersion with a maximum at 470 mμ [10, 11]; consequently, to establish whether the terpene contained in the group B fractions is β-pinene, its rotatory dispersion in the visible portion of the spectrum was calculated.

As is known, the specific optical rotation of a mixture of terpene hydrocarbons is additive (rule of Biot); consequently, the specific optical rotation of the investigated terpene for any wave length can be found from the equation

* The optical rotations for different wave lengths were measured on the Schmidt-Haensch three-pole polarimeter.

** $[\alpha]_\lambda$ of the 3rd fraction (camphene) in benzene (c = 44.76).

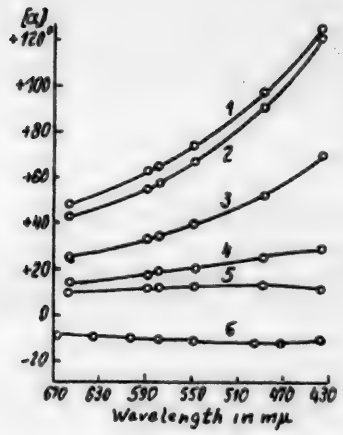


Fig. 2. Rotatory dispersion curves. 1) 15th fraction (d-limonene); 2) 3rd fraction (d-camphene), 3) 7th fraction (50% d-camphene + 50% of the investigated terpene); 4) 9th fraction (16% camphene + 84% of the investigated terpene); 5) investigated terpene (d-β-pinene, $[\alpha]_D$ + 10.8°); 6) l-β-pinene, $[\alpha]_D$ −10.8° [10, 11].

$$[\alpha]_\lambda = [\alpha']_\lambda \cdot \frac{a}{100} + [\alpha'']_\lambda \cdot \frac{100-a}{100},$$

where $[\alpha]_\lambda$ equals specific optical rotation of the corresponding fraction for a given λ; $[\alpha']_\lambda$ equals specific optical rotation of camphene, contained in the investigated fraction, for the same λ; a equals per cent of camphene in the investigated fraction; $[\alpha'']_\lambda$ equals sought optical rotation.

The values of $[\alpha]_\lambda$ and $[\alpha']_\lambda$ needed for the calculations are given in Table 1. The percent of camphene was analytically determined in the 7th fraction, in which connection a correction was made in the analysis result for etherification of the postulated β-pinene. From this data the rotatory dispersion of the investigated terpene, found in the 7th fraction, was calculated. Substituting $[\alpha]_D$ +10.8° in the above equation, the value calculated for the investigated terpene, the amount of camphene in per cent in the other fractions of group B can be found, and then the specific rotation of the investigated terpene, contained in these fractions, for the other wave lengths.

The rotatory dispersion of the investigated terpene, contained in different fractions, proved to be practically the same. This supports the validity of the assumption that the group B fractions are binary mixture of the investigated terpene with camphene. The absolute rotatory dispersion values of the investigated terpene agreed well with the absolute rotatory dispersion values for l-β-pinene [10,11] (Fig. 2); the optical rotation sign of the investigated terpene proved to be positive. The above made possible the conclusion that the investigated terpene is d-β-pinene.

The physical analysis results were confirmed by the oxidation of d-β-pinene with potassium permanganate to d-nopinic acid by the method of Dupont [12]. The yield of impure sodium nopinate from 1.92 g of the 8th fraction was 0.61 g (32%), and from 2.97 g of the mixed 9th and 10th fractions it was 0.75 g (25%).

The nopinic acid, recrystallized from water and dried at 45° had m.p. 126.5°. The mixed m.p. with l-nopinic acid failed to be depressed.

TABLE 2

Equilibrium Ratio Between α- and β-Pinenes in the Isomerizates Obtained from α-pinene at 160°.

Total amount of α- and β-pinenes in the isomerizate (%)	Amount of β-pinene in the isomerizate (%)	$K = \frac{\beta\text{-pinene}}{\alpha\text{-pinene}}$
46	0.82	0.018
32	0.48	0.015

d_4^{20} 0.8366, 0.0981 g sub.: 1.0010 g alcohol; α_D +0.50° (l = 50 mm); $[\alpha]_D$ +13.4°.

5.88 mg sub.: 14.06 mg CO_2; 4.735 mg H_2O. 11.9 mg sub.: 0.639 ml 0.1 N NaOH. Found %: C 65.25; H 9.01; equiv. wt. 186.2. $C_{10}H_{16}O_3$. Calculated %: C 65.19; H 8.75; equiv. wt. nopinic acid 184.2. (The elementary analysis was made by A. G. Khudovekova).

Based on the analyses, the equilibrium ratio between α- and β-pinenes in the isomerizates was determined. The basic principles used in calculating the amount of β-pinene in the different fractions obtained in the distillations, are given above. If α-terpinene was present in the analyzed fractions, it was first removed by treatment with maleic anhydride. The results for the determination of β-pinene in the different fractions were totalled. The data, obtained in the analysis of the two isomerizates, are given in Table 2.

SUMMARY

On heating with titanic acid there occurs interconversion of α- and β-pinenes with the establishment of dynamic equilibrium between the two isomers. The equilibrium is shifted toward the α-pinene.

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* See Consultants Bureau Translation, page 563

** See Consultants Bureau Translation, page 345.

COMMUNICATIONS TO THE EDITOR

In the journal Chem. Eng. News, 30, 4513 (1952) a report was published by the Nomenclature Committee of the Americal Chemical Society for the first half of 1952. In this report the term "arene" is proposed for the group designation of any aromatic hydrocarbon. In the report it is indicated that the term "arene" was originally proposed by E. J. Lawson.

To correct this error, I consider it necessary to mention that the term "arenes" for the designation of aromatic hydrocarbons was first proposed in the Soviet Union by the undersigned and was published as early as 1945 in the manual "Physico-Chemical Properties of Individual Hydrocarbons". First edition. Editor M. D. Tilicheev. Moscow-Leningrad State Sci.-Tech. Press, p. 25. 1945.

M. D. Tilicheev

In the paper of B. A. Arbuzov and N. P. Bogonostseva "The Reaction of Some Chloro and Bromo Derivatives With Sodium Diethyl Phosphite", published in the J. Gen. Chem., Suppl. II, 1144 (1953), an error appeared through the fault of the authors. In the experimental part, in describing the reaction of triethyl phosphite with diphenylbromomethane, it is indicated that a precipitate of sodium bromide is obtained, which is later removed by filtration.

Sodium bromide fails to be formed in the reaction with the triethyl phosphite. This description refers to the reaction with sodium diethyl phosphite and was erroneously made for the experiment with the triethyl phosphite.

All of the remaining data, including the numerical, are correct.

B. A. Arbuzov
N. P. Bogonosteva

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Composition and Chemical Properties of Magnesium Borides. P. 409.

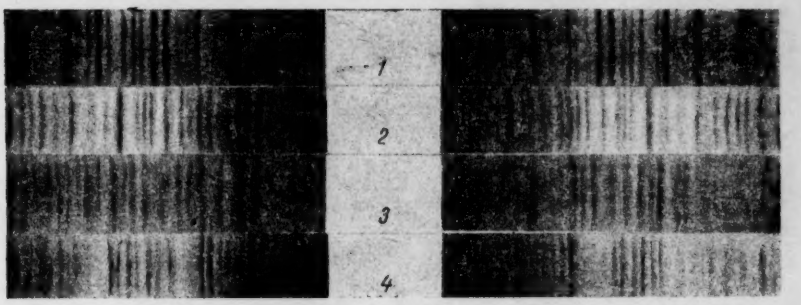

Fig. 1. Powder photographs of different boride phases.
1) MgB_2; 2) phase A; 3) phase B; 4) phase C.

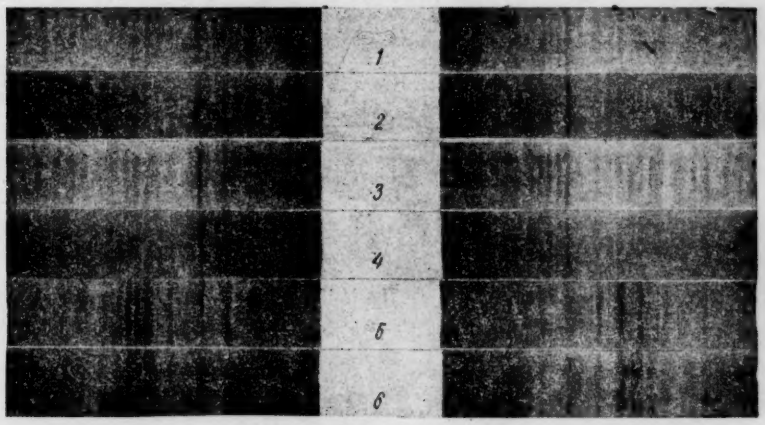

Fig. 2. Powder photographs of phase C. obtained under different conditions.
1) at 1200°; 2) at 1300°; 3) at 1500°; 5) at 1900°; 6) boron obtained by electrical discharge; 4) "crude" boron obtained by Moissan.

Singular Irreversible-reciptocal System with Separation of the Chlorides and Sulfates of Lithium and Thallium. P. 423.

Fig. 9. Three-dimensional diagram of the reciprocal system Li, Tl Cl, SO_4.